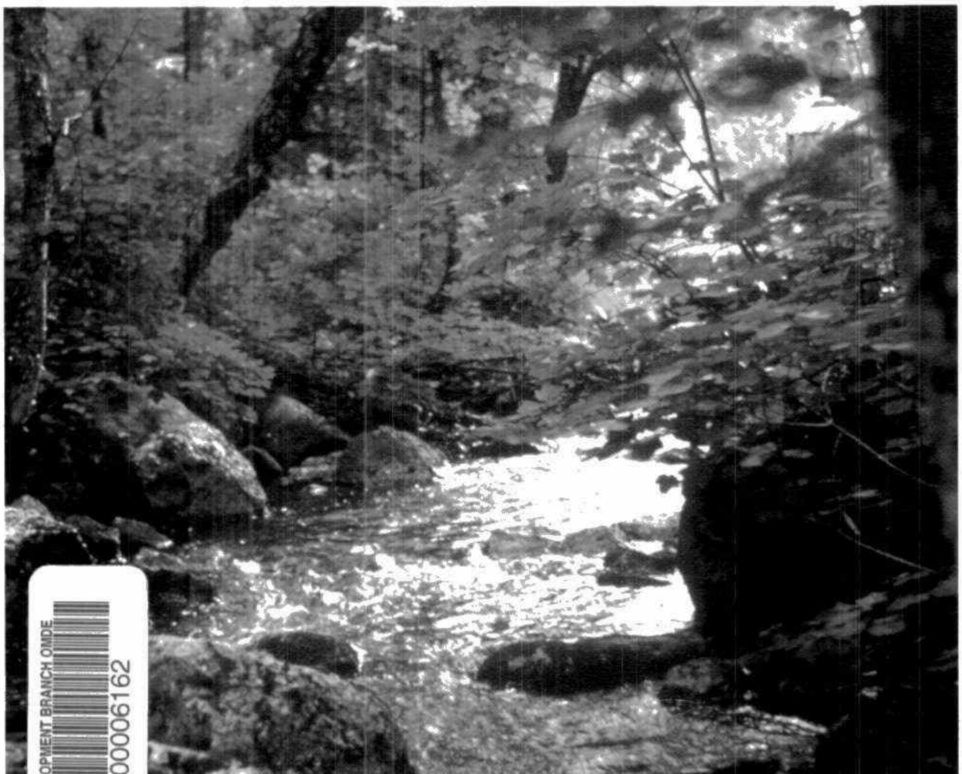
Federal/Provincial Research and Monitoring Coordinating Committee (RMCC)



THE 1990 CANADIAN LONG-RANGE TRANSPORT OF AIR POLLUTANTS AND ACID DEPOSITION ASSESSMENT REPORT

Part 8

QUALITY ASSURANCE STUDIES

1990

ACID RAIN

PLUIES ACIDES

Province of British Columbia
Ministry of Environment and Parks

Gouvernement du Québec
Ministère de l'Environnement

Alberta
ENVIRONMENT

New Brunswick
Department of Municipal Affairs and Environment

Saskatchewan Environment and Public Safety

Prince Edward Island
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Nova Scotia
Department of the Environment

Environment Ontario

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Department of the Environment

Canada

FEDERAL/PROVINCIAL

RESEARCH AND MONITORING

COORDINATING COMMITTEE (RMCC)

THE 1990 CANADIAN LONG-RANGE TRANSPORT OF AIR POLLUTANTS AND ACID DEPOSITION ASSESSMENT REPORT

PART 8

QUALITY ASSURANCE STUDIES

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PREPARED BY:

Editors

J. Lawrence, Research and Applications Branch, National Water Research Institute, Burlington, Ontario.

S. Villard, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario.

Overview on Quality Assurance in Aquatic Related Studies. (Section 8.2)

Anne Neary, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario.

Overview on Quality Assurance in Atmospheric Related Studies. (Section 8.3)

R.J. Vet, Atmospheric Environment Service, Downsview, Ontario.

Overview on Quality Assurance in Terrestrial Related Studies. (Section 8.4)

Jane Tims, Environment New Brunswick, Fredericton, New Brunswick.

Overview of Quality Assurance in Laboratory Studies. (Section 8.5)

K.I. Aspila, Research and Applications Branch, National Water Research Institute, Burlington, Ontario.

FOR THE QUALITY ASSURANCE SUBGROUP
OF THE RESEARCH AND MONITORING COORDINATING COMMITTEE

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8.1 SUMMARY

In 1982, a Memorandum of Intent (MOI) was jointly developed by scientists of the United States of America and Canada to address the issue of `Long Range Transport of Air Pollutants' (LRTAP). In this memorandum, the question of acid loadings to both countries was addressed. It was noted that the loading information provided by Canada and the United States differed significantly. Also, there were questions from various researchers as to the reliability of various data collected prior to 1980.

The Research and Monitoring Coordinating Committee (RMCC) established a number of working groups to address the issues of atmospheric, surface water, and terrestrial effects impacts due to acidic pollutants. At that time, the members of the RMCC recognized the need for a well designed quality assurance program to support the research and monitoring of the LRTAP studies and established a separate subgroup to address and promote quality assurance activities to ensure that good science was part of every study in the LRTAP Program.

During the period 1982 to 1990:

- The quality assurance subgroup was instrumental in developing the proposed siting (McQuaker 1982, and McQuaker et al., 1983), sampling (Sandberg et al., 1986), analytical (McQuaker, 1986, Campbell et al., 1985), and data reporting protocols (Still et al., 1983) for all the studies.

- The subgroup maintained close liaison with all of the studies in order to verify the adequate implementation of quality assurance procedures.

- The existence of the subgroup was instrumental in creating strong links with colleagues in the United States. As a result, a number of joint efforts were organized. These include analyst workshops, quality assurance for the Eulerian Model Evaluation Field Study and ecological quality assurance workshops.

The next four chapters chart the history, accomplishments and short-comings in the quality assurance program. In general where the studies dealt with quantifiable and semi-rigid analytical, sampling and databasing protocols, successful quality assurance was incorporated. When the measurements dealt with the response of biological systems, semi-quantitative sampling protocols, etc, with a few exceptions, the same degree of rigor in quality assurance techniques could not be applied.

The atmospheric and aquatic studies had a clear lead in developing quality assurance activities and as a result were able to respond to the requirements of an effective quality assurance program. As a result, the quality assurance programs in these studies have been able to address the measurement process more thoroughly.

In addition, the early activities of the Quality Assurance Subgroup tended to favour the aquatic and atmospheric studies and only in the mid 1980's, was more attention provided to the terrestrial component of the program. In as much as the terrestrial studies tend to have a greater ecological monitoring component, advanced quality assurance techniques to support such monitoring and research should be developed.

Aquatic Effects Studies

LRTAP aquatic effects studies in Canada are conducted through numerous federal and provincial government agencies. In many cases, the research evolved out of previous work, or was built into on-going aquatic studies. Often, historical data bases, as well as current data were used. As a result, a single QA/QC management plan or document outlining QA/QC procedures does not exist. Quality assurance/quality control activities, however, are very much an on-going aspect of all aquatic research and are built into all LRTAP related aquatic programs in Canada. Some of the QA/QC protocols were established for previous or other water monitoring programs and were retained, evaluated and continually updated for LRTAP research. Documentation is available, but is found in a large number of published and unpublished documents, and reflects the diverse nature of the research.

Canadian researchers recognize that a comprehensive QA/QC program is fundamental to good science. One drawback to the LRTAP aquatic effects research has been that it is conducted by numerous agencies at different levels of government. As a result the established QA/QC protocols were not necessarily the same between studies. It has only been through the coordinating role of the LRTAP Quality Assurance Subgroup and communications between individual scientists that the QA/QC activities are becoming standardized.

Information addressing all aspects of field and laboratory documentation, precision, accuracy, comparability, completeness and representativeness, is collected, stored and continually reviewed by the project managers, to ensure the validity of their findings and soundness of their conclusions. Overall the quality assurance protocols used in the LRTAP aquatic studies have proven effective to support the program and met individual project objectives.

Atmospheric Effects Studies

From the late 1970s to the late 1980s, the atmospheric research community has expended considerable effort on quality assurance and quality control. Most of this effort has gone into quantifying the accuracy, precision, comparability, completeness and representativeness of the atmospheric measurements, particularly, wet deposition measurements. The results of these activities indicate that wet deposition of the major acidifying species can be measured quite precisely (differences typically less than 5%) and with good comparability (± 25% between networks). Throughout the decade, site representativeness has improved in many Canadian networks, and data completeness has become an important factor in assessing the quality of wet deposition data.

While the atmospheric effects chapter has focused largely on quality assurance applied to the measurement of wet deposition, other types of measurement programs have also addressed quality assurance/quality control. This is apparent in the published literature, where almost all Canadian atmospheric research programs have considered quality assurance in their program structure and data analysis.

Terrestrial Effects Studies

Quality Assurance plans for LRTAP terrestrial components have been initiated but considerable work is still required to fully deploy the systems within all the terrestrial studies.

Terrestrial researchers utilizing water data components should consult the highly developed QA/QC methodologies established in precipitation monitoring or aquatic monitoring programs.

Additional work is required to establish means of determining accuracy of field measurements such as tree measurements, crown condition assessment and other physical measurements and a percentage of measurements and analyses should be repeated.

Laboratories should continue to develop in-house QA/QC programs, participate in interlaboratory comparisons and make widespread use of reference materials. Interlaboratory comparisons are essential for assessing data comparability.

Comprehensive field manuals provide personnel with the proper approaches to sampling and sample handling and allow continuity between investigators or support staff where the study extends beyond one season. Manuals should be developed before sampling commences and, where possible, tested during a pilot study (pilot studies need not be long if they are properly planned) to ensure that recommended methods are practical and finally modified for use in the field. Any changes in methodology should be documented and compared. In order to improve data representativeness, site selection criteria should

be established and documented before the commencement of a study. Once they have been chosen, study sites should be described and evaluated to document deviations from the established criteria. Any changes to sites during the course of the study should be documented.

Many of the measurements of the terrestrial effects studies require judgmental observations. In order to improve reliability it is necessary to develop new and appropriate techniques. These would include the use of multiple observers and specially trained observers.

Quality Assurance in Laboratory Studies

The external QA program presented to the LRTAP community by the QA subgroup of the RMCC has primarily addressed issues in the laboratory measurement process. In this area, the program has excelled and has had a positive impact. The presentation of one study every four months for eight years has provided the analyst with an atmosphere conducive to improvement and generated a heightened awareness of QA issues.

Evidence provided in each study has illustrated how many laboratories have clearly improved. Comparability of U.S. and Canadian data is viewed as excellent.

When the QA program was initiated in 1982, a data base management system was adopted to archive all pertinent QA information. It now contains almost a half million laboratory results and is viewed as a valuable resource.

The associated software has been instrumental in (a) creating laboratory specific performance appraisals, (b) demonstrating the long term stability of natural water samples and (c) illustrating the ongoing performance of each laboratory on a specific parameter or on a group of parameters. The data base has recently been used to illustrate how precision varies as a function of concentration. Specific criteria on performance specifications for future studies can now be set.

Although the external QA program has been effective, further areas need to be addressed. These include (a) the monitoring of field and sampling variances, (b) the discernment of laboratory measurement bias on a more absolute basis, and (c) more frequent studies on terrestrial substrates.

Overall

The quality assurance activities incorporated in all studies have had a significant impact in providing the Canadian Federal and Provincial governments with excellent data to support negotiations for emission reductions.

While a great deal has been accomplished in the atmospheric, aquatic and laboratory quality assurance programs a start has been made in installing quality assurance in terrestrial studies. This activity must be confirmed and enhanced during the expected monitoring phase on the impact of emission reductions.

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8.2 OVERVIEW OF QUALITY ASSURANCE IN AQUATIC RELATED STUDIES

8.2.1 INTRODUCTION

Long Range Transport of Air Pollutants (LRTAP) aquatic effects studies in Canada examine changes over time in the aquatic chemistry and biota due to the long range transport of air pollutants, with a focus on acid precipitation (Brooksbank et al., 1989). Most of this research is focused in Eastern Canada (Ontario, Quebec and the Atlantic provinces) where acid deposition rates are the highest.

In Atlantic Canada, LRTAP lake and river monitoring studies are coordinated by Environment Canada through a LRTAP monitoring network comprised of 78 lakes and 27 rivers. Monitoring stations were chosen based on data contained in the NAQUADAT files supplemented by results from surveys by Canadian Wildlife Service (CWS) (Kerekes 1973, Kerekes and Schwinghammer 1975) and Department of Fisheries and Oceans (DFO) (Scruton 1983, Kelso et al., 1986, Peterson et al., 1986). In addition, provincial data generated by regional water quality monitoring programs are incorporated into the data base. More detailed research concerning the acidification of catchments is carried out (by two levels of government and by academic institutions) in three lake basins in Kejimkujik National Park, Nova Scotia.

In Quebec, research is done at both the federal and provincial levels. The federal network is comprised of 41 stations (25 spatial and 16 temporal) chosen from an inventory study of 185 Canadian Shield headwater lakes in Quebec. These stations are located within a 150 km wide strip along the north shore of the St. Lawrence and Ottawa Rivers. More intensive research is focused on Lac Laflamme, a calibrated watershed in the Montmorency Forest area which is situated approximately 80 km north of Quebec city. A provincial lake data set of 1,091 lakes (compiled between 1981 and 1985) was used to calibrate an acidity model (Dupont and Grimard 1988, 1989). In 1986 a statistically-oriented lake monitoring network was established in order to quantify the status of lake acidification in southern Quebec (Dupont 1988, 1989). For this network, the area north of the St. Lawrence River and south of the 51st parallel was divided into five hydrographic regions. The Ministère de l'environnement du Québec has also completed more intensive toxicity work on four lakes in the Portneuf region of Quebec for comparison with lakes in the Adirondack region of New York (Simonin and Dupont 1986). Monitoring of some important salmon rivers along the north shore of the St. Lawrence River is also being done by the Canadian Department of Fisheries and Oceans (Walsh et al., 1987; Lachance et al., 1988).

In Ontario, lake surveys are coordinated by Environment Ontario. This has involved the sampling of over 6,000 lakes in the province between 1980 and 1988. These lakes, and their susceptibility to acidification, are listed in a report by Environment Ontario (1988). More detailed chemical and biological research on specific lakes and catchments is carried out by Environment Ontario in the Muskoka/Haliburton region (8 lakes, 24 catchments including biogeochemistry work on two of the catchments - Plastic and Harp Lake) and until 1988, in the Thunder Bay region (Hawkeye Lake)). Environment Canada and the Federal Department of Fisheries and Oceans also conducts research in the Algoma area (Turkey Lakes) and the Kenora area (Experimental Lakes Area).

Less research is conducted in western Canada, as most of the sensitive western aquatic sites are in areas of low acidic deposition. Currently, a joint Environment Canada/Saskatchewan Environment monitoring study involves sampling 22 lakes in the Shield area of northern Saskatchewan. Some LRTAP-related aquatic effects research is also underway in the Pacific coast region of British Columbia under the direction of the B.C. Ministry of Environment, the Department of Fisheries and Oceans and Environment Canada.

All the above studies involve a spatial and/or temporal sampling network with defined sampling stations and times, sample collection, handling and analysis, and data reporting, storage and interpretation. An effective QA/QC program, therefore, must address each of these componenets. For all of the above programs, study sites and sampling stations have been defined and documented and the siting criteria used to ensure representativeness. This applies whether the samples are lake, stream, groundwater or precipitation. Deviations from the siting criteria are documented and justified. Instrument operation, sample collection, sample handling and analysis and data reporting procedures are defined, documented and regularly reviewed and updated. Protocols for personnel training have been developed, and estimates are made of data variability with changes in personnel assigned to a task.

Accuracy, precision, representativeness and completeness of the data are monitored through field QC programs which include field blanks, field replicate sampling (spatial and temporal), split samples, blind audit samples, standard additions etc. and laboratory QC programs include within-run and between-run replicate samples, calibration standards and checks, laboratory intercomparison samples, known reference samples, method blanks and interference, sensitivity and recovery checks. Data managers apply predetermined guidelines and tests for the inclusion or exclusion of outliers and anomalous data.

In order to help evaluate the completeness of the QA/QC activities for the various aquatic programs, a summary of these activities is presented in Table 8.2.1.

TABLE 8.2.1
QA ELEMENTS FOR THE CANADIAN AQUATIC LRTAP STUDIES

Study Name	Type	Formal QA Plan	Data Qlty Object.	Source of Error	Data Valid Proced.	Pilot Studies	Manual (Field)	Manual (Lab)	Lab Plan	Field Blanks	Field Rep. to Lab.	Blind Audit to Lab.	Interlab Compar.	Sple Repres. Evalu.	Collect Method	QC Data Evalu.
Atlantic Canada																
St.John River	river monitor.	D	Y	Y	B	N/A	B	B	I	D	D	N/A	B	I	D	D
N.S. LRTAP Lakes	lake monitor.	B	N/A	Y	B	N/A	B	B	I	B	B	N/A	B	D	D	D
Nfld. LRTAP Lakes	lake monitor.	B	N/A	Y	B	N/A	B	B	I	B	B	N/A	B	D	D	D
LRTAP Overview Rivers	river monitor.	D	N/A	Y	B	N/A	B	B	I	D	D	N/A	B	D	D	D
Kejimkujik	calibr.w/shed	D	N/A	Y	B	N/A	B	B	I	D	D	N/A	B	D	D	D
DFO Newfoundland	lake survey	B	N/A	Y	B	Y	B	B	B	B	B	N/A	B	B	B	D
DFO Maritimes	lake survey	B	N/A	Y	B	Y	B	B	B	B	B	N/A	B	B	B	D
DFO Labrador	lake survey	B	N/A	Y	B	Y	B	B	B	B	B	N/A	B	B	B	D
U of Minn.	lake survey	I	N/A	Y	B	N/A	N/A	B	I	D	D	N/A	N/A	I	D	D
Environ. Labrador	lake survey	I	N/A	Y	B	N/A	B	B	I	D	D	N/A	B	I	D	D
Quebec																
Environ. Quebec Network																
- Spatial	lake survey	N	I	I	Y	B	Y	Y	Y	Y	Y	N	Y	Y	I	I
- Temporal	lake survey	N	I	I	Y	B	Y	Y	Y	Y	Y	N	Y	Y	I	I
Quebec Environment	lake survey	Y	Y	I	Y	N	Y	Y	Y	Y	Y	Y	Y	Y	I	Y
Lac Laflamme																
- Ion Budget	calibr.w/shed	N	I	I	Y	N	N	N/A	Y	N	N	N	D	Y	N	I
- Spring Melt	calibr.w/shed	N	I	I	Y	N	N	N/A	Y	N	N	N	Y	Y	I	I
Ontario																
Provincial Lake Survey	lake survey studies	I	Y	Y	Y/D	Y	I	Y/B	Y/I	D	Y/D	N	Y/D	D	D	D
Plastic/Harp/Hawkeye Lakes	calibr.w/shed	Y	Y	Y	B	Y	D	B	B	D	D	D	D	D	B	D
Biological Studies	lake/stream	Y	Y	Y	Y	Y	D	B/D	Y	D	D	D	D	D	B	D
Chemical Studies		Y	Y	Y	Y	Y	D	B/D	Y	D	D	D	D	D	D	D
Turkey Lakes	calibr.w/shed	D	I	Y	Y	N	N	Y	D	N	D	I	D	D	N	D
Experimental Lakes Area	calibr.w/shed	I	I	I	Y	N	N	Y	D	Y	Y	Y	Y	Y	Y	Y

Y yes
N no
B initiated before the existing study
D initiated during the existing study
I informally considered
N/A not available

8.2.2 EVOLUTION OF AQUATIC-RELATED QUALITY ASSURANCE ACTIVITIES IN THE PAST DECADE

Atlantic Canada:

Monitoring for water quality in Atlantic Canada has evolved over many years. The most comprehensive program dates from the early 1950's (Thomas, 1953). Documentation at that time established siting criteria, sampling and shipping protocols as well as analytical criteria. Data validation techniques included ion balance routines, mass balance measurements (theoretical vs. measured dissolved solids), theoretical specific conductance calculations and a recognition that all those criteria failed in the case of low ionic strength waters that contain significant quantities of organic acids. Advances in analytical methodology (Thomas, 1960; Environment Canada 1974, 1979) as well as sampling methods (Thomas 1960; Environment Canada 1972, 1973, 1983) have been documented periodically. Those procedures, combined with the Environment Canada round robin program which addressed laboratory precision and accuracy, served to ensure the integrity of the program.

In 1984, a consistent, documented field QA/QC program was established which would be followed routinely by all field personnel. The program involved documentation of all field procedures, including siting criteria (Clair et al., 1986), triplicate sampling of at least 15% of all samples, sample filtration, preservation and blank preparation at the end of each sampling day, and shipment of the samples to the laboratory within 48 hours of collection (Arseneault and Howell, 1987). The triplicate sampling program was applied to the five major aquatic studies: (1) International St. John River; (2) Nova Scotia LRTAP Lakes; (3) Newfoundland LRTAP Lakes; (4) LRTAP Overview Rivers; (5) Kejimkujik Calibrated Basin (Arseneault and Howell 1985). The siting criteria for the studies (listed in Clair et al., 1986) recognized that samples were also collected from many of the stations for non-LRTAP purposes (Howell and Brooksbank, 1987).

The first step toward data management QA was the incorporation of the surface water data collected by the various agencies into NAQUADAT, Environment Canada's National Water Quality data base.

This data base includes surface water quality data for the Atlantic provinces collected by at least seven different government agencies. Although the data had been evaluated through the internal QC procedures of each agency, additional QC protocols were applied prior to the use of this data for LRTAP purposes (see 8.2.3). Protocols were also established for the handling of duplicate and triplicate analyses.

Quebec:

In Quebec, concern over the acidification of surface waters on the Canadian shield led to the establishment, in 1983, of a federal network to detect spatial and temporal trends in surface water quality. The QA/QC activities developed hand in hand with the program to ensure that the program objectives would be met successfully. Information from an inventory data set of 185 lakes in the province was used to arrive at a rational network design which would allow the desired objectives to be met with maximum efficiency and limited resources (Bobee, et al., 1983, 1986; Haemmerli et al., 1985). The development of siting criteria for the study lakes is described in Bobee et al., (1983) and Brooksbank et al., (1989). Since the detection of temporal trends in a particular site does not depend upon the same statistical characteristics as those determining the spatial evolution of surface water quality, the spatial and temporal aspects were considered independently and a network was developed which was a compromise between the two (Bobee et al., 1983, 1986, Haemmerli et al., 1985). Decisions on the number of temporal sites required over a 5 or 10-year period to detect a trend were based on work done by Lettenmaier (1977) and Berryman (1984). As some basic assumptions had to be made in order to design the network, these assumptions were later verified with data from the first year's sampling. Tests for representativeness, homogeneity and stability are described in Haemmerli et al., (1985).

Sampling procedures and protocols were adapted from Environment Canada (1983). These, as well as analytical methodologies, are outlined in Haemmerli (1988). Recommendations for field quality control checks such as the submission of replicate samples and field blanks are given in Brooksbank et al., 1989. A field triplicate sampling program was designed for the monitoring network. Laboratory analyses conform to standard methods outlined in Environment Canada (1979) and Environment Canada (1981), and are conducted at the National laboratory in Burlington, Ontario and the regional laboratory in Longueuil, Quebec. The National laboratory has documented internal QA/QC protocols and also participates in external interlaboratory quality assurance checks specifically for LRTAP samples. All data undergo validation procedures which are described in 8.5 and, once validated, the data are entered into the NAQUADAT central data bank.

The lake acidity monitoring network (ReSSALQ) designed by the Ministère de l'Environnement du Québec takes into account both chemical and biological aspects of the effects of acidification.

The chemical surveys have established protocols for site selection, precision estimation and sampling and data validation (Dupont 1988, 1989, Dupont in press). In all, 1273 lake stations are monitored according to a five year recurrent program, in which 200 to 337 lakes are visited each year. A field triplicate sampling is performed on 5% of all samples taken. All samples are analyzed at the Ministère de l'environnement du Québec laboratory according to standardized protocols. A QA/QC plan exists for the laboratory which

includes field blanks, lab blanks, calibration standards and checks, performance monitoring and intermethod assessment (Ministère de l'Environnement du Québec 1986). This laboratory also participates in the Federal-Provincial LRTAP interlaboratory quality assurance program. Data are stored in the BQMA data bank (Banque de la Qualité du Milieu Aquatique) which will accept only data which fit into a given range of values. Data outside the range are checked manually. These data are transferred each year into the NAQUADAT data bank. Quality control is also performed at the data treatment level with validation techniques such as ionic balance, conductivity deficit vs ionic deficit, logical comparison between pairs of variables, etc. These methods are described in Dupont (1986, 1988).

The biological studies, which are also part of the ReSSALQ network, are conducted in order to assess the effects of acidity on fish populations and fish communities. In each hydrographic region surveyed, 30 to 74 lakes are sampled according to standardized field protocol. This protocol, along with the siting procedure is described in Tremblay (1989). Validation procedures are performed in order to detect data anomalies and are discussed in 8.2.3.

Ontario:

LRTAP-related research in Ontario is conducted through both federal and provincial agencies. Environment Ontario, through the Acid Precipitation in Ontario Study (APIOS), examines the effects of acidification on the aquatic environment. These studies are based primarily in the Muskoka/ Haliburton region of Ontario at Dorset, although some work has been done near Thunder Bay and Sudbury. The aquatic studies are comprised of: 1) a chemical component which includes chemical limnology, lake and stream modelling, metal contaminants and lake surveys; 2) biological studies which involve investigations on algae, zooplankton and toxicity levels, biological monitoring and metal and organic residue monitoring; and 3) remedial lake methodologies. This LRTAP-related aquatic research began in 1979 and evolved out of an earlier aquatic research program (the Lakeshore Capacity Study). Hence, much of the current QA/QC program has been in place since 1975 and has expanded as the program has grown (Locke 1985; Locke and Scott 1986; Locke, in press).

Study design and siting criteria have been defined and documented for the Lakeshore Capacity Study (Dillon et al., 1986). Deviations from the siting criteria were documented and justified. Appropriate lakes from this group were identified and retained for LRTAP related work due to their ideal location and site characteristics and the valuable historical data base which was available. Additional lakes were chosen which were susceptible to acidification (Locke and Scott 1986). Sampling equipment and methodologies for water and biological samples were documented (McQuaker et al., 1983; Scheider et al., 1983; Locke and Scott 1986). A preliminary intensive replicate study was undertaken and later a routine design was established.

Environment Ontario's Laboratory Services Branch, is the analytical support group for the APIOS Aquatic Effects program. It also has an established QA/QC program (Moody 1983, Environment Ontario 1985, 1986). This is continually evaluated and updated by laboratory staff, and includes measurements of accuracy and precision, interference and recovery checks, blind audit samples, and interlaboratory and intermethod comparisons. All laboratory methods are documented in detail (Environment Ontario 1983) and performance reports are released (Environment Ontario 1980, 1984, 1986, 1987, 1989a, 1989b). In addition to the routine QA/QC protocols, the laboratory participates in external quality assurance checks specifically for LRTAP samples through the LRTAP interlaboratory intercomparison studies (see Section 8.5).

Analytical and field data from the Muskoka/Haliburton and Thunder Bay area studies and some of the Sudbury studies are stored on the ORACLE data base management system. The data base includes sample location and description as well as the analytical method used for each result. Chemical data are processed using a data editing program that assists in error and inconsistency identification and data base modification capabilities are user restricted. The data are also checked for order of magnitude errors or obvious contamination. Atmospheric data play a key role in examining chemical and hydrological budgets of watersheds. Many sources of meteorological data are used and stored on the data base system at Dorset. The data sources and applications for utilizing the data are described in Locke and deGrosbois, (1986).

For the algal studies all sampling and mapping procedures are documented and mapping procedures are compared between technicians with regular recalibration of observational data (Jackson pers. comm.). All collection and laboratory procedures, as well as taxonomic work, are performed according to referenced procedures (see for example Bulletin of the Buffalo Society of Natural Sciences, 1981; Nicholls, K. 1978, 1979, 1980, 1984a, 1984b).

Biological studies involving zooplankton collection use documented methods which were established and tested prior to the LRTAP-related aquatic work. These methods are described in Scheider et al., (1975) and Yan (1979). Quality control protocols for the biological work evolved over the past decade with the growth of the Acid Precipitation study.

In the Algoma region north of Sault Ste. Marie, water chemistry data have been collected by Environment Canada for 4 lakes (Turkey Lake, Little Turkey Lake, Wishart Lake and Batchawanna Lake). Lake surveys have also been carried out south of the Turkey Lakes and in Pukaskwa National Park. Siting criteria and rationale for the work at Turkey Lakes is described in Jeffries et al., (in press) and sampling and data processing methods are discussed in Jeffries et al., (1983) and Semkin et al., (1987).

In the Kenora region of Ontario, the Department of Fisheries and Oceans has sampled 12 lakes annually. In 1968, an Experimental Lakes Area was established for lake eutrophication studies. Many of the quality assurance activities were developed and documented at this time and siting criteria are described in Brunskill and Schindler (1971). The intention of setting aside the Experimental Lakes Area was to permit whole lake and watershed manipulations. These lakes have been used to examine the effects of acidification on aquatic systems (Schindler 1980).

As evidenced by the above summary, LRTAP related aquatic research in Canada is carried out by numerous provincial and federal agencies. The Research and Monitoring Coordination Committee (RMCC) Quality Assurance Subgroup ensures the integrity of this research by bringing together provincial and federal representatives. Research conducted by Environment Canada occurs within a sound quality assurance policy and plan which establishes formal responsibility and accountability on the part of research staff, numerous documents outline QA procedures and guidelines to be followed (Environment Canada 1983, Gaskin 1988a, 1988b, Agemian 1988, Brooksbank et al., 1989). Communication between federal and provincial agencies is evident in the recommended protocols for water sampling outlined in Brooksbank et al., (1989). This document makes reference to related work done by Environment Ontario. Finally, all Canadian laboratories analyzing LRTAP aqueous samples must use analytical methods which have received prior approval from the RMCC Quality Assurance Subgroup (Campbell et al., 1985).

8.2.3 RESULTS OF AQUATIC RELATED QUALITY ASSURANCE ACTIVITIES IN THE PAST DECADE

8.2.3.1 Quality Assurance Activities Related to the Determination of Accuracy:

The accuracy of a measurement requires that both laboratory and field personnel know and can quantify the sources of uncertainty in a measurement. Quality assurance related to the accuracy of field measurements and sample collection in the Canadian aquatic programs involves detailed documentation of: site and station selection criteria and procedures, the use of field equipment, sample collection and treatment and field quality control protocols (Environment Canada, 1983; Scheider et al., 1983; Haemmerli 1988; Locke 1985; Clair et al., 1986; Locke and Scott 1986; Arseneault and Howell 1987; Brooksbank et al., 1989). These written instructions combined with training of all field

personnel (see for example Clair et al., 1986) ensure that field measurement and sampling errors are kept to a minimum. In addition to personnel training and documentation of procedures, the regular submission of field blanks (including container blanks, filter blanks and sampler blanks) are also used to help isolate sources of contamination. Accuracy in the field applies not only to sample collection but also to any field measurements made.

The national and provincial laboratories use analytical methods which have been tested, validated and documented over the last ten to fifteen years (Environment Canada 1974, 1979, 1981, 1983; Environment Ontario 1983; Ministère de l'environnement du Québec 1982). The quality assurance activities related to the determination of the accuracy of an analytical measurement involve quality control protocols which include calibration, sensitivity and interference checks, control charting, blanks, blind audit samples and spiked samples (Environment Ontario, 1989a, 1989b; Algemian, 1988).

External accuracy checks on the analytical laboratory are made by comparing field measurements of a relatively stable parameter (eg. specific conductance) with the laboratory measurement. Results of such a study are listed in Brooksbank et al., 1989, Gaskin 1988.

All Canadian and many U.S. labs analyzing LRTAP samples participate in the National Water Research Institute's interlaboratory comparison for LRTAP samples. Although this provides a measure of precision and not accuracy, the median value (result) used for comparison approaches the "true" (accurate) value as the number of participants increases (see Section 8.5). Analytical methods have also been compared between the Ministère de l'environnement du Québec and the New York State Department of Environmental Conservation (NYSDEC) Rome Field Station (Simonin and Dupont 1986) (see Table 8.2.2).

As methods and instrumentation continually improve, it is realized that historical data may be inaccurate for specific parameters. An example of this is the early 1980 introduction of ion chromatography (IC) for the measurement of sulphate in aqueous samples. The use of IC for sulphate determination eliminates the interference caused by sample colour when the methylthymol blue (MTB) colourimetric procedure is used. As IC came into routine use, it was recognized that this procedure provided a more accurate measurement of sulphate on coloured water samples. Studies were, therefore, undertaken to examine the accuracy and comparability of the historical sulphate data (Cheam et al., 1984, Howell and Pollock 1985, Green et al., 1986, Locke, in press).

TABLE 8.2.2
COMPARISON OF TWO LABORATORIES: MINISTERE DE L'ENVIRONNEMENT DU QUEBEC AND THE NEW YORK STATE DEPARTMENT OF ENVIRONMENT.
(FROM: SIMONIN AND DUPONT 1986).

Results of a paired Student's t-test comparing the analytical results from the two laboratories for six variables in each of the study lakes.

Lake	pH	Colour	Alkalinity	Calcium	Conductivity	Total Aluminum
Quebec Lakes						
Bleu	0	**	0	0	0	0
Edithe	0	**	0	0	**	0
Main De Fer	0	*	0	0	*	0
Poliquin	0	**	0	0	*	0
New York Lakes						
Big Moose	0	**	0	0	0	*
Moss	0	**	0	0	0	0
North	0	**	0	*	0	0
South	*	**	0	0	0	

0 no significant difference between laboratory results at *alpha* = 0.05
* significant difference at *alpha* = 0.05 to 0.02
** highly significant difference at *alpha* ≤ 0.01

Possible solutions to dealing with incomparable data sets include: 1) continuing to use the old, but inaccurate, method: 2) adopting the more accurate method and discarding the old data (not really a viable alternative when looking for trends through time); 3) changing the old data to match the new through the application of a correction factor and 4) changing the new data to match the old (see for example Howell and Pollock 1985). The latter two alternatives require that the laboratory capacity is such that large numbers of samples can be analyzed by both methods in order to come up with correction factors for each site. Other studies have been done which evaluate the accuracy of commonly used methods when applied to Canadian Shield softwater systems (see for example Stainton 1980, Jeffries and Zimmerman 1980, Herczeg et al., 1985).

Perishability studies on samples have also been conducted by various agencies to examine the accuracy of a particular test on samples which may not be analyzed immediately (Locke, in press). The known perishability of certain parameters resulted in the establishment of field laboratories for the analysis of tests such as pH, alkalinity, nitrogen compounds and dissolved oxygen and inorganic carbon. Non-perishable tests were and continue to be performed at central laboratories. Field measurements of perishable parameters such as pH are also made and compared with the laboratory measurement as a check on sample integrity when it arrives at the lab (Howell, 1986).

Data validation techniques are employed by all project managers to determine sources of uncertainty in the data. These include the calculation of ion balances, equivalent major ion concentrations, standard deviations, theoretical specific conductance vs. measured conductivity, sum of the constituents, 95% confidence intervals and sea salt corrected (excess) concentrations of sulphate (Green et al., 1986;, Howell and Brooksbank 1987). Criteria for the acceptance or rejection of data based on these calculations and the history of analytical method consistency were developed. Data are scanned for obvious contamination or order-of-magnitude errors.

In addition to calculated vs measured conductivity and ion deficits, the Ministère de l'environnement du Québec also uses a data screening technique whereby only data falling within a certain range of values or Z scores is accepted (Dupont pers. comm). The rejected data are checked manually. For biological studies in Quebec, length-weight relationships are calculated for each fish species for each lake. Points lying outside accepted values are eliminated. Environment Ontario data also includes pH vs alkalinity comparisons, theoretical alkalinity calculations using dissolved inorganic carbon and pH, comparisons of total nitrogen and total phosphorus, and cation/anion charge balances with and without metals and an estimate of organic anions. For some data sets, comparisons of three alkalinity measurements (fixed endpoint 4.5 and 3.8 and Gran alkalinity) are made and sodium (Na) and chloride (Cl) plots are prepared (Dillon pers. comm.).

8.2.3.2 Quality Assurance Activities Related to the Determination of Precision:

Field quality assurance activities related to precision measurements consist primarily of replicate sampling protocols. For example, in 1984 in Atlantic Canada, a triplicate sampling program was established for all LRTAP-related aquatic work. An average of 15% of all water samples are collected in triplicate and this may be as high as 25% in projects with a small number of stations (Arseneault and Howell, 1985). These triplicates provide a measurement of the reproducibility of the data (field and lab error combined). In Quebec, Environment Canada and the Ministère de l'environnement du Québec use similar triplicate sampling programs. From 1983 to 1986, Environment Ontario collected between three and ten samples in addition to the regular sample at 54 sites (including lake, stream and precipitation sites) on a rotating basis. The mean, standard deviation, coefficient of variation and number of samples were recorded for each chemical parameter, for each lake, stream, precipitation and lake profile site. In 1986, three sites were chosen to continue replicate sampling (Locke, in press).

The analytical laboratories also examine the precision of their methods. Quality control protocols in the provincial and federal laboratories require measurements of within-run and between-run precision. Samples in the run are analyzed in duplicate during the run and quality control solutions are analyzed with every run to provide a measure of between-run precision (see for example Agemian 1988, Moody 1983, Environment Ontario 1989a, 1989b). Blanks and spiked samples run with each batch and more than once throughout the run. This process also provides measures of precision. Between laboratory precision is measured by the federal LRTAP interlaboratory comparison study (see Section 8.5).

8.2.3.3 Quality Assurance Activities Related to the Determination of Comparability:

Comparability of data which has included an analytical method change is a problem for scientists involved in long term monitoring studies. Whenever a major method change occurs, data comparability studies are undertaken. As discussed in 8.2.3.1, the most important of these method changes has been the switch from sulphate determination by the MTB colourimetric procedure to measurement by ion chromatography.

The method for colour measurement has been changed in some laboratories from the measurement of "apparent" colour (including turbidity) to the measurement of "true" colour (dissolved coloured substances only). True colour has also been determined by more than one method. Possible differences between methods prompted comparability studies (Simonin and Dupont 1986, Haemmerli 1988, Locke, in press). Other method changes

have occurred as new instrumentation becomes available with improved detection limits (Locke, in press). Canadian researchers realize the importance of exercising caution in the interpretation of long term data sets and the need for documentation of method changes, including the date of change. Good communication between the laboratory and the project manager is an essential prerequisite to obtaining interpretable results.

Often, the data generated are used by scientists for comparison with research done at other institutions within Canada or in other countries. The LRTAP interlaboratory comparison study ensures method comparability in Canada and with some agencies in the United States. The LRTAP Quality Assurance Subgroup recommends analytical methodologies. Some method development has been done in Canada comparing various methods mentioned in scientific publications (Jeffries and Zimmerman 1980, Stainton 1980, Clair and Komadina 1984, Herczeg et al., 1985, Lazerte et al., 1988). In addition to analytical method comparability, an overlap period is required if field methods change (sample collection or field measurement methods).

Examples of changes in field measurement methods include: the estimation of the euphotic zone by Secchi disc and by light profile using a quantum sensor (Locke, in press), and the measurement of stream flow by current meter, calculation using velocity and cross-sectional area of the stream and by catching the entire volume of the stream for a measured period of time and calculating discharge.

Sample collection methods may also change and the data generated before and after these changes must be compared. Examples of these types of comparisons include work on zooplankton collection by the Department of Fisheries and Oceans (Schindler 1969) and Environment Ontario (Yan and Strus 1980). More recent and extensive comparisons of zooplankton collection methods used in Canada will be presented at the 1990 Society of Chemical Limnologists Workshop. Comparisons of water collection methods have also been done (Dupont 1986; Locke, in press). In addition, many unpublished studies were conducted prior to the collection of field data and samples to ensure data comparability.

8.2.3.4 Quality Assurance Activities Related to the Determination of Completeness and Representativeness of Sample Collection and Analytical Data:

Completeness and representativeness of data encompasses everything from the region under investigation to the types of analytical tests done, the number of samples analyzed and the data validation techniques used. A complete and representative data set is crucial to successfully achieving the goals and objectives of the study and arriving at scientifically valid conclusions and recommendations. Most LRTAP-related aquatic programs in Canada had preliminary, and have continuing, studies which address this aspect of a particular sampling program.

An informative summary discussing the establishment of Canadian LRTAP aquatic monitoring programs is given in Brooksbank et al., (1989). Initially, all regions chosen for study were selected so as to represent the areas which are the most threatened by acidification. Mean sulphate and alkalinity data are given in Table 8.2.3.

Sets of defined and documented siting criteria (Brunskill and Schindler 1971; Bobee et al., 1983; Dillon et al., 1986; Dupont and Grimard 1988, 1989; Dupont 1988, 1989; Jeffries et al., (in press)) ensure that the sites selected are representative of the aquatic resources in each particular region. Examples of the number of sites required to be representative of a region are given in Dupont (1988, 1989). In some cases, lakes for which a sound historical data base existed were chosen. This meant that siting criteria were initially developed for purposes other than LRTAP (Thomas 1953; Howell and Brooksbank 1987; Locke and Scott 1986). In these cases, the location and analytical data base for these sites were evaluated to ensure that they were appropriate for LRTAP aquatic effects monitoring.

The detection of spatial trends in acidification may not depend on the same characteristics as the detection of temporal trends and, therefore, if one monitoring network is designed to address both aspects, a rational procedure for network design must be followed. One example of an approach used in Canada to combine two such networks is given in Bobee et al., (1983) and is summarized in Haemmerli et al., (1985). As the study progressed, statistical tests on the data were used to determine the homogeneity of sites within given zones and the representativeness of the sites. Through this continual evaluation some sites were eliminated and others added.

The sampling frequency and the number of samples taken from a particular station depend on the objectives of the program and the magnitude of change to be detected. A general description of this is given in Gaskin (1988b) and Brooksbank et al., (1989). By considering only those sampling times which minimize the variability in certain parameters (eg. fall turnover of the lakes) the magnitude of change which is statistically significant may be lowered. An example of this is given in Table 8.2.4. These data, shown for Lac Laflamme, indicate much less variability in the monthly means for alkalinity and sulphate during the fall season than during the other months or as reflected by the annual means. Sampling, therefore, may be optimized by concentrating on the fall season (Brooksbank et al., 1989). Other considerations, however, must also be taken into account. For example, alkalinity is the highest during this time of year and biased sampling may result if the sampling design is not carefully thought out (Dillon pers. comm.). Further examples of the number of samples and sampling frequency required for various Canadian LRTAP studies are given in Table 8.2.4 and Fig. 8.2.1, and the types of calculations involved are given in Haemmerli et al., (1985) Dupont (1989) and Scholer et al., (1990). For biological studies, the optimum number of samples to be representative, minimize variability and yet be feasible given the available resources, is also determined prior to routine sampling. One approach to determining this is given in Yan and Stokes (in press) and shown in Fig. 8.2.2.

Eliminating spatial variability at a sampling site (e.g. whether or not the sampling location or depth at a station accurately represents the water fraction or area intended) is also a concern of the project manager. Studies addressing this problem are done prior to selection of the actual sampling depth or location. Environment Ontario tested sampling stations for each sample type (inflow, outflow, stream, groundwater, precipitation) to ensure that the sample was representative of the study site. For example, in 1980, five lake outflow sampling sites were tested to see whether samples taken at the outflow control structure (the usual point of outflow sampling) were, in fact, similar in chemistry to samples taken at the point where the lake meets the outflow. From the results of this study it was decided to move one of the sampling locations (Locke, in press). Sampling equipment and collection methods have also been evaluated (McQuaker et al., 1983, Scheider et al., 1983, Locke and Scott 1986, Ryan and Kerekes 1989). Knowledge of the spatial variability of a species in the water body is especially important in biological studies if representative data are to be obtained. An example of such a study for zooplankton was done by Yan (1986) and is shown in Table 8.2.5. The depth of sampling in a lake is important and is often monitored by accompanying temperature and conductivity profiles (Howell 1986; Locke 1989). Compositing of samples taken over time is also used to address temporal variability at a specific site.

The analytical parameters examined must also be relevant and sufficient to address the goals and objectives of the study. Often the list of analytical tests evolve as the data become available and are evaluated. A list of essential parameters for the Canadian LRTAP program is given in Brooksbank et al., (1989). Other parameters may be region-specific and done only by certain agencies. Reports on the findings of LRTAP studies usually list the chemical and/or biological parameters measured and the methods which were used.

TABLE 8.2.3

Lac Laflamme (From: Brooksbank et al., 1989).

Mean Annual Concentrations of Sulphate and Alkalinity for Lac Laflamme, Quebec.

	Alkalinity (mg/L)		Sulphate (mg/L)	
	Mean	Std. dev.	Mean	Std. dev.
Lac Laflamme				
1981	5.085	2.256	4.644	1.417
1982	5.308	1.173	3.735	0.446
1983	5.422	1.280	4.052	0.350
Overall	5.336	1.390	4.144	0.954

Note: Samples collected weekly.

Finally, the data validation techniques are especially important to ensure complete and representative data sets. Dealing with "less than" values and the possibility of eliminating anomalous data which may in fact be real are problems which are crucial to the integrity of the data base. All Canadian LRTAP researchers use a stringent set of data screening techniques for the inclusion or exclusion of data, and data slated for exclusion are always checked manually prior to their elimination.

8.2.4 SUMMARY

LRTAP aquatic effects studies in Canada are conducted through numerous federal and provincial government agencies. In many cases, the research evolved out of previous work, or was built into on-going aquatic studies. Often, historical data bases, as well as current data were used. As a result, a single QA/QC management plan or document outlining QA/QC procedures does not exist. Quality assurance/quality control activities, however, are very much an on-going aspect of all aquatic research and are built into all LRTAP related aquatic programs in Canada. Some of the QA/QC protocols were established for previous or other water monitoring programs and were retained, evaluated and continually updated for LRTAP research. Documentation is available, but is found in a large number of published and unpublished documents, and reflects the disparate nature of the research.

Canadian researchers recognize that a comprehensive QA/QC program is fundamental to good science. The LRTAP Quality Assurance Subgroup of the Research and Monitoring Coordinating Committee ensures excellent lines of communication between federal and provincial agencies, and maintains analytical uniformity through recommended analytical methods and the National interlaboratory intercomparison study for LRTAP samples.One drawback to the LRTAP aquatic effects research has been that it is conducted by numerous agencies at different levels of government. As a result the established QA/QC protocols were not necessarily the same between studies. It has only been through communication between scientists that the QA/QC activities are becoming standardized.

Information addressing all aspects of field and laboratory documentation, precision, accuracy, comparability, completeness and representativeness, is collected, stored and continually reviewed by the project managers, to ensure the validity of their findings and soundness of their conclusions. Overall the quality assurance protocols used in the LRTAP aquatic studies have proven effective to support the program and met individual project objectives.

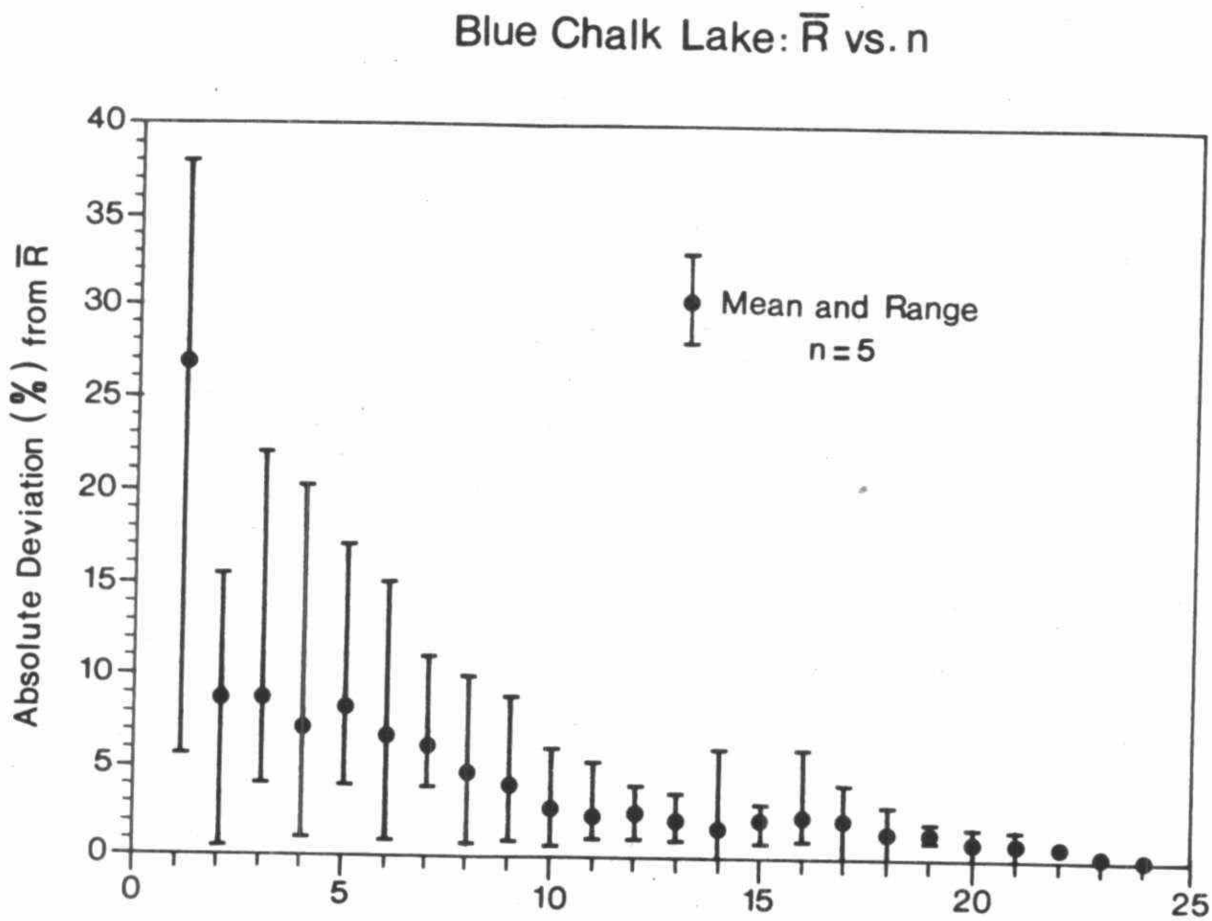

FIG. 8.2.1 **Influence of Sampling Frequency on Mean Richness ($\bar{R}$) Estimates of Zooplankton (Yan 1986).**

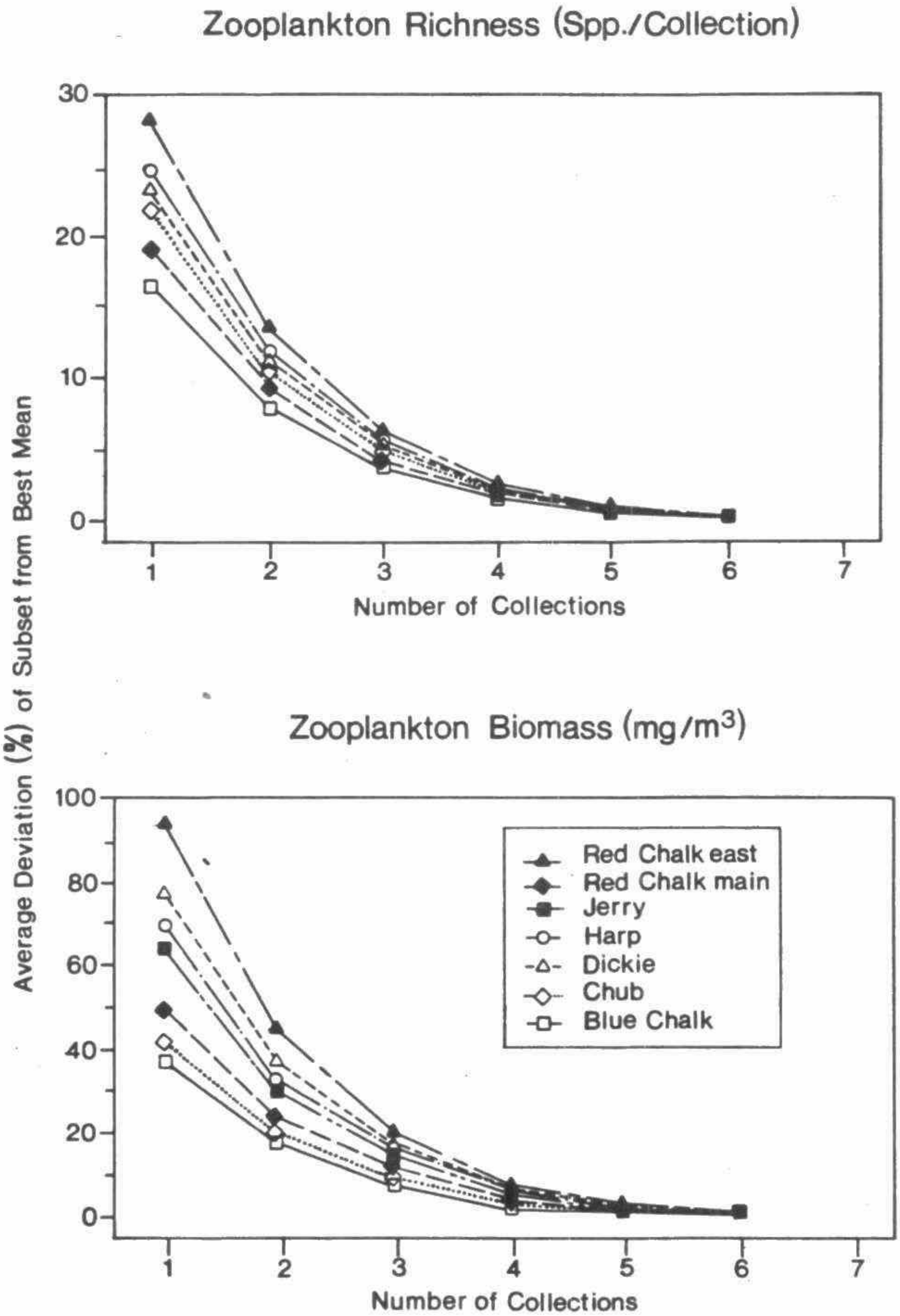

FIG. 8.2.2 Subset Size Required to Minimize Varability in Zooplankton Richness and Biomasss. (From: Yan and Stokes, 1989).

TABLE 8.2.4a

Number of Water Samples Required from a Lake Network to Ensure Representativeness (From: Brooksbank et al., 1989)

Number of Water Samples Required Each Year from the Lake Network to Detect a Change in the Levels of Alkalinity and Sulphate at 95%, 90%, and 80% Confidence Levels.

	Alkalinity			Sulphate		
Confidence Level (%)	increment (mg/L) 0.5	1	1.5	increment (mg/L) 0.5	1	1.5
Southern Nova Scotia (N = 88)						
95	39	10	5	61	16	7
90	33	9	4	51	13	6
80	26	7	3	40	10	5
Newfoundland (N = 70)						
95	76	19	9	120	30	14
90	53	14	6	84	21	10
80	33	9	4	51	13	6

TABLE 8.2.4b
Mean Monthly Sulphate Values (mg SO_4^{-2}/L) for Lac Laflamme
(From: Brooksbank et al., 1989)

Month	1981 N	1981 Mean	1981 Std. Dev.	1982 N	1982 Mean	1982 Std. Dev.	1983 N	1983 Mean	1983 Std. Dev.
January	4	4.375	0.395	4	3.475	0.457	4	4.350	0.100
February	4	4.050	0.580	4	3.450	0129	4	4.300	0.082
March	5	7.400	1.742	5	3.480	0.227	5	4.180	0.249
April	4	4.975	0.299	4	3.650	0.370	4	4.225	0.499
May	4	6.050	0.173	4	3.500	0.271	5	3.600	0.200
June	5	6.020	0.110	5	3.840	0.378	4	3.825	0.330
July	4	4.500	1.158	4	4.150	0.342	4	4.325	0.275
August	5	3.860	0.089	5	3.600	0.200	5	4.020	0.277
September	4	3.525	0.150	4	3.375	0.050	4	4.050	0.173
October	4	3.400	0.231	4	3.450	0.058	4	3.950	0.238
November	4	3.525	0.310	5	4.200	0.200	5	3.760	0.230
December	5	3.500	0.316	4	4.600	0.377	4	4.200	0.516

TABLE 8.2.4c
Mean Monthly Alkalinity Values ($CaCO_3$ mg/L) for Lac Laflamme
(From: Brooksbank et al., 1989)

Month	1981 N	1981 Mean	1981 Std. Dev.	1982 N	1982 Mean	1982 Std. Dev.	1983 N	1983 Mean	1983 Std. Dev.
January	4	6.275	0.189	4	8.325	0.419	4	5.950	0.645
February	4	5.100	3.030	4	9.025	0.457	4	6.750	0.351
March	5	4.120	2.402	5	9.180	0.766	5	7.340	0.760
April	3	5.733	1.537	8	8.275	1.022	4	6.500	0.990
May	4	3.875	1.034	4	4.875	1.053	5	4.120	0.622
June	5	2.280	0.835	5	4.500	0.406	4	3.625	0.472
July	4	2.375	0.640	4	4.725	0.250	4	3.825	0.472
August	4	3.025	0.350	5	5.300	0.745	4	4.675	0.492
September	4	4.600	0.497	3	4.967	0.751	4	5.000	0.346
October	4	5.175	0.550	4	5.950	0.252	4	5.125	0.096
November	4	5.200	0.668	5	4.580	0.973	5	5.540	0.404
December	5	7.520	0.432	4	5.375	0.550	4	6.425	0.287

TABLE 8.2.5

SPATIAL VARIABILITY OF SESTON IN RED CHALK LAKE
(Yan, 1986)

	Seston concentration (mg/m^3)						
	1	2	3	4	5	*F* Ratio	C.V. %
June 9	69[a]	81	105	82	76	3.27	16
July 21	139	127	113	115	101	5.66**	12
July 28	118	106	118	111	84[b]	2.10	13
August 5	136	131	127	130	131	0.50	10
August 12	126	116	113	125	133	0.62	7
August 25	85	81	73	82	91	1.48	8
September 8	63	78	77	75	82	1.24	10
September 22	108	121	123	158	151	4.43*	16
October 5	109	107	107	102	101	1.16	3
October 23	129	149	165	172	--	4.46*	8
November 11[c]	236	245	226	221	280	13.24**	10
Mean	108.2	109.7	112.1	115.2	105.0		

[a]In duplicate: all other stations in triplicate.
[b]Excluded from ANOVA because of heterogeneous variance.
[c]High numbers on November 11 were probably attributable to resuspension of bottom sediments after autumnal overturn. These values were not included in the mean.

Arithmetic mean of seston (>76 μm) concentration from triplicate tows from each of five stations (1-5) in Red Chalk Lake in 1981. *F* ratios from one-way analyses of variance are included. Single and double asterisks indicate significant station effects at P = 0.05 and 0.01, respectively. Coefficient of variation (C.V.) for stations means is also indicated.

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8.3 OVERVIEW OF QUALITY ASSURANCE IN ATMOSPHERIC RELATED STUDIES

8.3.1 INTRODUCTION

From the late 1970s to the late 1980s, atmospheric research into the long range transport of air pollutants focused on three atmospheric processes -- transport, conversion, and deposition. By far, the largest effort has concentrated on the measurement of regional precipitation chemistry and wet deposition. To this end, the Government of Canada and most provincial governments have installed and operated wet deposition monitoring networks within their jurisdictions. The names of these networks, their sponsoring agencies, and the years of operation are summarized in Table 8.3.1. The effort spent on other atmospheric measurements, e.g., regional air chemistry, dry deposition, fog/cloud water deposition, has also been significant but less so than on network measurements of wet deposition.

Throughout the decade, numerous papers, reports and conference proceedings have been published from Canadian air and precipitation network measurements. These include studies into the spatial and temporal distribution of wet deposition in Canada, investigations into atmospheric transport and conversion of acidifying species, and research into the terrestrial and aquatic effects of acid precipitation. Additional research has also been carried out on cloud chemistry, long distance dispersion, fog or cloud water deposition, ozone production, ozone transport, and long range transport model testing.

As the amount of atmospheric research increased throughout the past decade, so too did concern over the quality of that research. It was in response to this concern that quality assurance/quality control programs became an essential part of atmospheric research programs. This chapter reviews and summarizes the most important quality assurance activities undertaken within the decade. By necessity, it emphasizes the quality assurance of wet deposition measurement programs (particularly networks) since most atmospheric research in the decade focused on wet deposition, and most of the published quality assurance information applies to wet deposition.

8.3.2 A HISTORY OF QUALITY ASSURANCE ACTIVITIES IN ATMOSPHERIC RESEARCH

As atmospheric research proliferated in the late 1970s and the 1980s, quality assurance became an accepted and necessary element of most atmospheric research programs. One of the earliest quality assurance activities was the development and publication of siting criteria for wet deposition monitoring sites. This was first done in 1980 for the

TABLE 8.3.1
CANADIAN WET DEPOSITION MONITORING NETWORKS

NETWORK ACRONYM	NETWORK NAME	OPERATING PERIOD
CANSAP	Canadian Network for Sampling Precipitation	1977 - 1983
APN	Canadian Air and Precipitation Network	1978 - 1983
CAPMoN	Canadian Air and Precipitation Monitoring Network	1983 - present
BCPCSN	British Columbia Precipitation Chemistry Sampling Network	1984 - present
APQMP	Alberta Precipitation Quality Monitoring Program	1978 - present
MAPMN	Manitoba Acid Precipitation Monitoring Network	1984 - 1986
APIOS-C	Acidic Precipitation in Ontario Study - Cumulative Network	1980 - present
APIOS-D	Acidic Precipitation in Ontario Study - Daily Network	1980 - present
REPQ	Réseau d'échantillonnage des précipitation du Québec	1981 - present
NBPN	New Brunswick Precipitation Network	1981 - present
NSPMN	Nova Scotia Precipitation Monitoring Network	1980 - present
NPMN	Newfoundland Precipitation Monitoring Network	1987 - present
EPSN	Environmental Protection Service Network	1981 - present
GLPN	Great Lakes Precipitation Network	1969 - present

Ontario APIOS network (Vet, 1980), and again in 1982 for Canadian networks in general (McQuaker et al., 1982). McQuaker et al., (1982) also made other significant contributions to the field of quality assurance by recommending acceptable procedures for the collection, handling and analysis of wet deposition samples. A similar report for snow sampling was published in 1986 by Sandberg et al., (1986).

Some of the other quality assurance activities undertaken within the decade include:

- The upgrade of several federal and provincial wet deposition monitoring networks to improve siting and operations, e.g., in 1983, the conversion of Environment Canada's Canadian Network for Sampling Precipitation (CANSAP) and Air and Precipitation Network (APN) to the upgraded Canadian Air and Precipitation Monitoring Network (CAPMoN) (Vet et al., 1983), and the upgrade of monitoring sites in the Réseau d'échantillonnage des précipitation du Québec (Grimard, 1984).

- The development and implementation of formal Quality Assurance Programs within existing deposition monitoring networks, e.g., APIOS networks (Bardswick, 1984; CSC, 1985), CAPMoN (Vet and Onlock, 1983), New Brunswick (NBDMA&E, 1989), and the Chemistry of High Elevation Fog (CHEF) network (EAG, 1987). Mills (1986) also produced a generalized Quality Management Plan for use in Canadian LRTAP research programs (Mills, 1986).

- The operation of intercomparison studies between federal and provincial networks, and Canadian and US networks. These included both instrument intercomparisons (Chan et al., 1984; Vet and Onlock, 1981) and network intercomparisons (Vet et al., 1981; Bigelow et al., 1984; Vet, 1988).

- The operation of laboratory intercomparison studies between federal, provincial, and US laboratories involved in wet and dry deposition research (see section 8.5)

- The development of standard methods for: (1) calculating wet deposition from precipitation chemistry data, and (2) evaluating the representativeness of wet deposition measurements based on data completeness statistics and site representativeness ratings (UDDBC, 1985).

These activities supplemented the routine quality assurance and quality control activities carried out in most measurement programs. The most significant of all quality assurance/quality control results are described in the following sections.

8.3.3 RESULTS OF ATMOSPHERIC-RELATED QUALITY ASSURANCE ACTIVITIES

The quality assurance activities address five basic elements of quality assurance, namely, accuracy, precision, completeness, representativeness and comparability. The following describe the major QA/QC results obtained over the past decade organized according to the five elements.

8.3.3.1 Quality Assurance Activities Related to Accuracy:

Accuracy is defined as the degree of agreement between a measurement and an accepted or true value (USEPA, 1980). Unfortunately, most atmospheric QA activities cannot quantify the true accuracy of a measurement system - simply because true values of precipitation and air chemistry are unknown and unmeasurable. As the next best alternative, most programs attempt to quantify the accuracy of specific parts of the measurement method. For example, wet deposition programs which cannot determine the true accuracy of their wet deposition measurements can determine the accuracy (or inaccuracy) of specific components of the method, such as the effects of evaporation and dry contamination.

The most comprehensive research on component accuracy was carried out by Environment Ontario in the early 1980s (Chan et al., 1985). It was found that, for 28 day sampling periods, evaporative losses in APIOS precipitation samples were generally less than 10% and dry contamination effects (caused by the entry of dry material) were up to 11% for calcium and 31% for magnesium. Dry contamination of H^+, sulphate and nitrate was found to be very low.

In another study, Chan et al., (1983) investigated wet deposition measurement errors caused by the absorption/ desorption of metals at collection vessel walls. They found that new polyethylene bags used to collect precipitation samples did not desorb trace metals (from the bag walls into solution), but did absorb (out of solution) measurable amounts of Al and Zn (roughly 20%) within one day and large amounts of Cd, Fe, Cu, Zn and Al (26-47%) within 28 days. The net result of the absorption effect was to produce a negative error in the measurement results. Acid leaching to quantify the amount of absorbed material helps to compensate for this error.

Finally, Bardswick et al., (1986) investigated errors in the APIOS wet deposition measurement system due to field and laboratory sample handling. They found negligible dry contamination of daily samples for all analytes except Cl^-, K^+, Ca^{++}, and Na^+, for which minor contamination was found in approximately 15% of field blanks.

They also found chemical instability and sample degradation of known concentration samples as they travelled through the field and laboratory measurement systems.

Within the chemical laboratory, McQuaker (1986) investigated the accuracy of various analytical methods for measuring the acidity and alkalinity of precipitation. He concluded that alkalinity can be determined reasonably well by several methods, namely Gran's titration, an extrapolation technique, and inflection point titration. He also concluded that total acidity should not be measured using the Gran's titration method unless specific conditions are met, (McQuaker, 1986). McQuaker and Sandberg (1988) carried this work further by defining acceptable laboratory control limits for Gran's titrations and ion balances in precipitation samples.

In summary, the last decade has seen considerable quality assurance activity related to determining the accuracy of wet deposition measurement systems. The work quantified various component errors, and resulted in the introduction of measurement techniques to reduce such errors.

8.3.3.2 Quality Assurance Activities Related to Precision:

Precision is defined as a measure of mutual agreement among individual measurements of a property, usually under prescribed similar conditions (USEPA, 1980). Within the decade, two daily wet deposition networks, (APIOS and CAPMoN), determined the precision of their precipitation chemistry measurements by operating duplicate collectors at several of their sites. The results are presented in Table 8.3.2. Note that the mathematical expressions for precision are different for the two networks.

Table 8.3.2 shows that the two networks have similar levels of precision. For example, the precision of pH, $SO_4^=$, and NO_3^- was very good (typically within 6%) while the precision of Na^+,Cl^-, Ca^{++},and $Mg^{++}$was moderate to low (within 20%). Perfect precision occurred for several species, an artificial result caused by laboratory precision being approximately equal to the overall measurement precision.

The use of collocated instruments for measuring overall precision is now commonplace in several Canadian networks, e.g., CAPMoN, APIOS and Quebec. In mid-1988, APIOS and CAPMoN also began making similar collocated measurements with their air chemistry (filter pack) systems.

TABLE 8.3.2
THE PRECISION OF DAILY PRECIPITATION CHEMISTRY MEASUREMENTS FROM SEVERAL SITES IN THE APIOS AND CAPMoN NETWORKS

Measurement	Precision (%)				
	APIOS[a]			CAPMoN[b]	
Sample Depth	2.1,	3.2,	8.3	0.0,	3.7
pH (Lab)	--	--	--	0.2,	0.2
H^+ (Lab) Concentration	6.9,	6.9	11.5	--	--
$SO_4^=$ Concentration	2.7,	3.6,	5.8	2.5,	3.2
NO_3^- Concentration	2.7,	3.1,	10.7	2.3,	2.2
Cl^- Concentration	11.2,	12.2,	8.2	9.1,	7.7
NH_4^+ Concentration	5.6,	6.7,	3.2	3.1,	3.1
Na^+ Concentration	22.5,	13.9,	0.0	0.0,	0.0
Ca^{++} Concentration	15.9,	11.4,	20.7	11.1,	5.6
Mg^{++} Concentration	15.5,	0.0,	75.0	0.0,	0.0
K^+ Concentration	25.9,	22.5,	29.2	0.0,	0.0

a. $100 \times$ median of $\frac{\text{absolute between-sampler difference for sample i}}{\text{concentration of single sample i}}$.
From Chan et al. (1985).

b. $100 \times 1.05 \times \frac{\text{(median of absolute between-sampler differences)}}{\text{(median of collocated average concentrations)}}$.
From Vet and Sirois (1987).

8.3.3.3 **Quality Assurance Activities Related to Comparability:**

Comparability is defined as the confidence with which one data set may be compared to another (USEPA, 1980). It is often referred to as 'relative accuracy', or the bias between similar measurement systems. In the last decade, considerable quality assurance activity has focused on measurement comparability (rather than accuracy) because it is easy and extremely important when combining data sets from different deposition networks.

Comparability studies in Canada began in the early 1980s. The first was an APIOS network study in which monthly APIOS wet deposition measurements were compared to monthly measurements from the CANSAP and GLP networks (Vet et al., 1981). In the study, APIOS sampling instruments were collocated at 10 CANSAP and GLPN sites. It was concluded that the CANSAP measurements of $SO_4^{=}$, NO_3^-, Na^+, Cl^-, Ca^{++}, Mg^{++} and K^+ were significantly higher (at the 95% significance level) than the APIOS measurements. The differences were attributed to higher evaporative losses and to dry contamination in CANSAP samples - both the result of poor bucket seals on the CANSAP collectors. APIOS measurements were not found to be significantly different than GLPN measurements for most of the major ions (except pH) on an annual basis; however, significant summer to winter differences were found. As a result of the study, Environment Ontario decided to implement the APIOS network across the province, rather than relying on the existing CANSAP and GLP networks for data.

Several other comparability studies were undertaken in the 1980s. They include:

- A 3-year (1981-1983) comparison study between the Canadian CANSAP network and the United States National Atmospheric Deposition Program (NADP) network. In this study, wet deposition samplers from the two networks were collocated at three sites in Canada and three sites in the US. Preliminary results indicate a bias toward higher concentrations in the CANSAP network (Bigelow, 1984). As with the previous study, the bias appears to be due to evaporative losses and dry contamination in the CANSAP collectors.

- An ongoing intercomparison study between Environment Canada's CAPMoN network and provincial wet deposition monitoring networks. CAPMoN collectors were collocated with the provincial collectors at a minimum of one site in each province. The results up to 1986 are summarized in Vet (1988) and illustrated in Figure 8.3.1. In general, they show that CAPMoN and provincial precipitation-weighted mean SO_4^{-2} concentrations are comparable within a range of -12% to +32%. In fact, with the exception of one ratio, all of the provinces' annual concentrations fall within the ±25% of the CAPMoN concentrations, and two thirds fall within ±15%. As a result, CAPMoN/provincial comparability for sulphate is considered to be quite acceptable and has led to the merging of federal and provincial data sets within the Canadian National Atmospheric Chemistry Data Base (NAtChem).

- An on-going intercomparison study between the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the US National Atmospheric Deposition Program/National Trends Network (NADP/NTN). This study began in 1986 with the objective of quantifying biases between the two countries' wet deposition measurements. The study was (and is still) carried out at one site in each country -- Sutton, Quebec and Penn State University, Pennsylvania. A preliminary analysis of the first two years of data is published in Vet et al. (1989). The results indicate that, in general, the concentration data from the two networks track each other very well (see Figure 8.3.2). However, statistically significant differences at the 95% confidence level were found for ammonium, nitrate, and hydronium ion concentration, sample depth, and standard gauge depth (see Table 8.3.3). CAPMoN values exceeded the NADP/NTN values for all of these parameters.

The biases between the two networks are generally small. For example, the relative bias (i.e., the ratio of the bias to the mean concentration value) is less than 10% for nitrate concentration and standard gauge depth, approximately 15% for hydronium ion concentration, and roughly 25% for the concentration of ammonium. The study concludes that data from the two networks are comparable but caution must be exercised when comparing ammonium from the two networks.

Round-robin intercomparison studies have been presented to those laboratories involved in analyzing wet and dry deposition samples. These studies, known as the LRTAP Interlaboratory Comparison Studies, have been carried out three times per year since 1983. A discussion of the results is given in section 8.5 (note that wet and dry deposition laboratories make up only a fraction of the laboratories taking part in these intercomparisons). Since 1988, Environment Ontario's APIOS laboratory and Environment Canada's CAPMoN laboratory have also been participating in a monthly laboratory intercomparison study between several Canadian and US laboratories. The results to-date indicate very high comparability between these laboratories (differences generally less than 5% for sulphate and nitrate).

In summary, considerable effort has been expended to date to quantify the comparability of wet deposition networks within Canada and between Canada and the United States. The results show that between-network differences do exist, largely because of differences in measurement systems and protocols. Although the data are generally comparable to within ± 15%, biases as high as 25 to 30% do exist for certain networks and species.

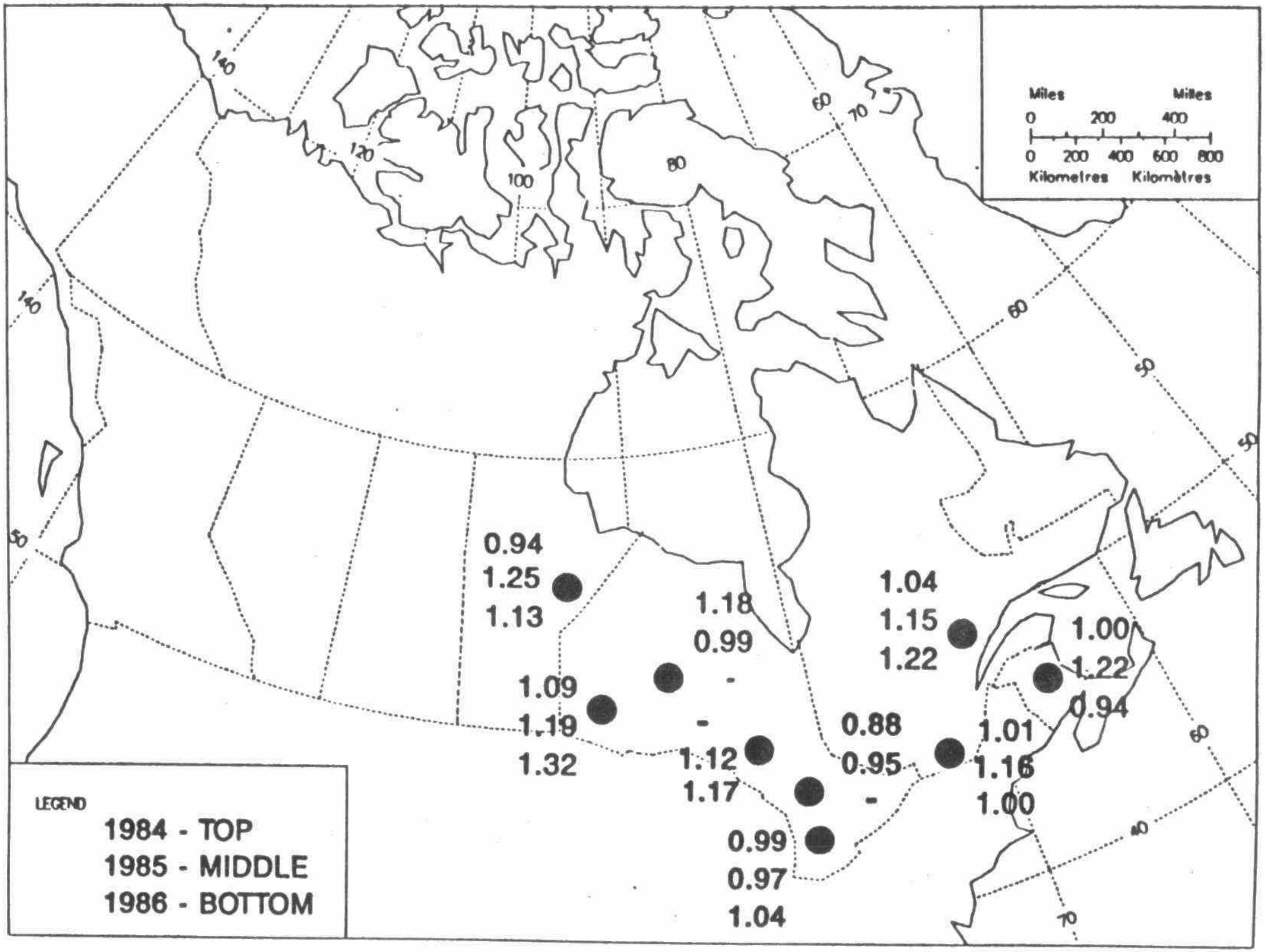

Fig. 8.3.1 RATIO'S (Provinces/CAPMon) of annual precipitation-weighted mean sulphate concentration at collocated provincial and CAPMoN sites for years 1984 (top), 1985 (middle), and 1986 (bottom).

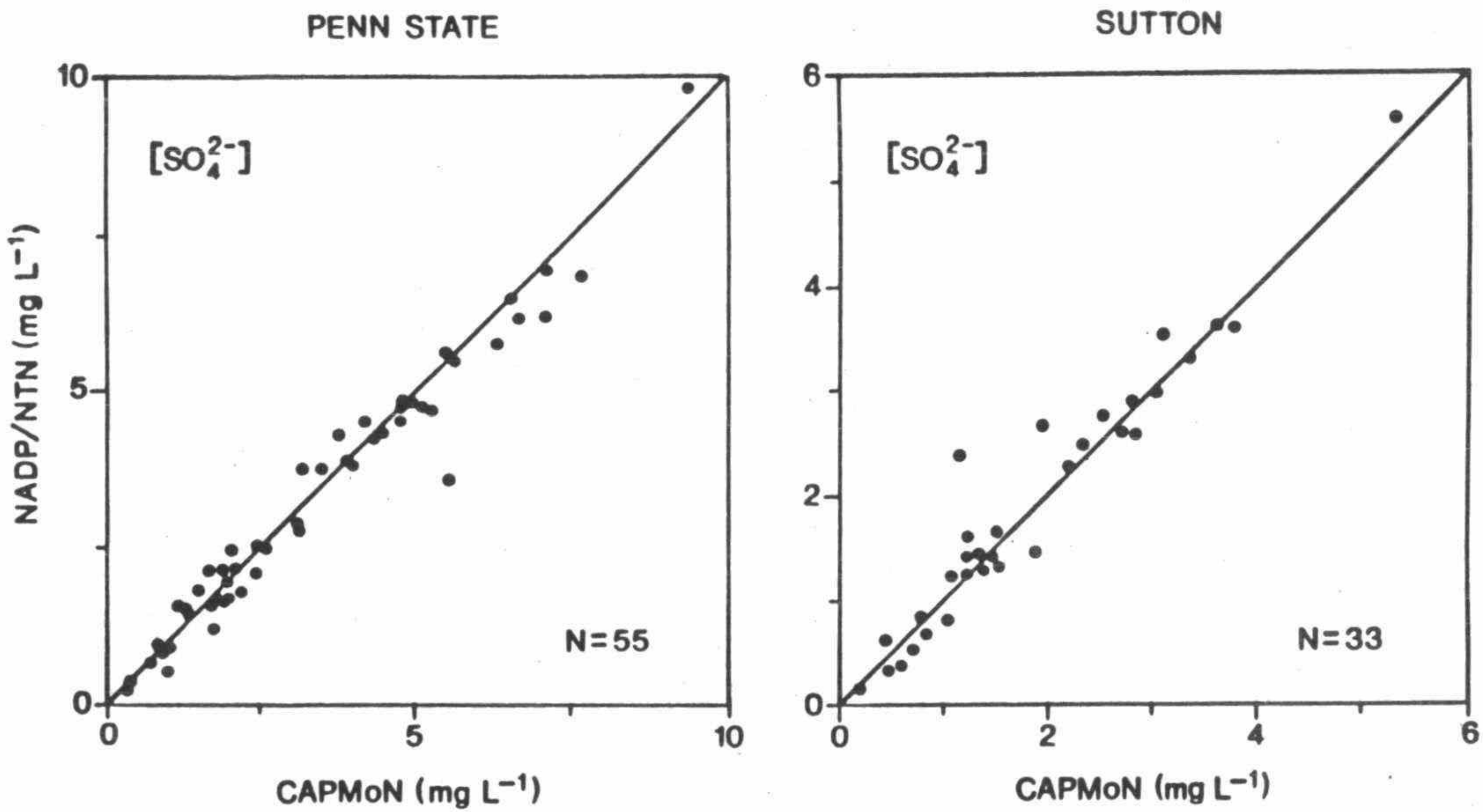

Fig. 8.3.2 Scattergrams of CAPMoN and NADP/NTN Sulphate Concentrations. (from Vet et al., 1989).

8.3.3.4 Quality Assurance Activities Related to Completeness:

Data completeness is defined as the amount of valid data obtained from a measurement system compared to the amount expected (USEPA, 1980). In 1985, the RMCC Unified Deposition Data Base Committee (UDDBC) defined five measures of data completeness for wet deposition data (see UDDBC, 1985). They also defined three levels of data quality based on the completeness of the data. The levels ranged from high quality (Level 1) to low quality (Level 3) depending on the percentage of data available. Since then, the US Acid Deposition System (ADS) data base has adopted the practice of rating the quality of Canadian and US wet deposition data according to the UDDBC completeness levels. Other scientific studies have also adopted the UDDBC completeness criteria, e.g., the International Sulphur Deposition Model Evaluation (Clark et al., 1987).

As of 1985, the Canadian Air and Precipitation Monitoring Network (CAPMoN) adopted the practice of publishing annual wet deposition estimates only if certain UDDBC data completeness criteria are met. At the same time, CAPMoN implemented a corrective action system which maximizes data capture at all wet deposition sites. Several provincial networks have adopted similar practices.

8.3.3.5 Quality Assurance Activities Related to Representativeness:

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population at a sampling point (USEPA, 1980). The characteristic of concern to air and precipitation chemistry monitoring is the regional representativeness of the measurement sites, in particular, a site's ability to produce air and precipitation samples affected only by long distance sources of pollution.

Regional site representativeness became a major concern in 1980, at which time the Ontario APIOS network developed a set of objective siting criteria for selecting wet deposition monitoring sites (Vet, 1980). In 1982, McQuaker et al., (1982) produced a set of siting criteria for general application to Canadian wet deposition monitoring networks. These criteria received widespread acceptance and use by most provinces.

Most networks which began operations in the early 1980s used siting criteria similar to those of McQuaker et al., (1982). Since then, many networks have undergone formal audits of their measurement sites specifically to assess their regional representativeness. For example, the Canadian Network for Sampling Precipitation (CANSAP) underwent several audits in the early 1980s (Concord Scientific Corporation, 1981; Vet et al., 1982). Based in part on the results, CANSAP underwent a complete redesign in 1983 and became the Canadian Air and Precipitation Monitoring Network (CAPMoN). As part of the conversion, almost all CANSAP sites were closed and new, regionally-representative sites were opened.

The Ontario APIOS network also underwent several formal audits in the 1980s (e.g., Concord Scientific Corporation, 1983) which resulted in the upgrading and relocation of many sites. In 1984, the Réseau d'échantillonnage des précipitations du Québec carried out an internal site representativeness review which resulted in the resiting and upgrading of many sites (Grimard, 1984), and, in 1989, the Manitoba Acid Precipitation Monitoring Network underwent an evaluation of its former measurement sites in preparation for reinstatement of the network.

Concern over the regional representativeness of wet deposition measurement sites has had an impact on the management and analysis of Canadian wet deposition data. In 1985, the RMCC Unified Deposition Data Base Committee (UDBBC) formulated a set of siting criteria against which major North American network sites were evaluated (UDDBC, 1985). The criteria (Table 8.3.4) were used to rate the representativeness of all measurement sites as:

Level 1 - regionally-representative,
Level 2a - potentially regionally-representative,
Level 2b - potentially non-regionally-representative,
Level 3 - non-regionally-representative.

These site ratings are incorporated into the US Acid Deposition System (ADS) data base and the Canadian National Atmospheric Chemistry (NAtChem) data base. As such, they have been used to select regionally-representative data for producing deposition statistics and/or maps. For example, the wet deposition maps shown in the RMCC 1990 Acid Rain Assessment document are based on data vetted for site representativeness. Other studies, such as the International Sulphur Deposition Model Evaluation (Clark et al., 1987), have also used the UDDBC ratings to assess site representativeness when selecting data for scientific study.

In general, site representativeness has been, and continues to be, a major concern of all Canadian air and precipitation chemistry networks. Audits and inspections of measurement sites have been carried out in most networks, followed in many cases by site upgrades and relocation. Since the mid-to-late 1980s, users of wet deposition data have recognized the importance of site representativeness and now use the available site information when vetting their data.

TABLE 8.3.3

ESTIMATES OF BIAS BETWEEN CAPMoN AND NADP/NTN PRECIPITATION CHEMISTRY MEASUREMENTS (FROM VET ET AL., 1989)

MEASUREMENT	BETWEEN-NETWORK BIAS[1]	
	Sutton, Quebec	Penn State University Scotia, PA.
SO_4^{-2}	-0.04	0.02
$N\text{-}NO_{3-}$	0.01	0.04[2]
Cl^-	-0.02	0.00
Ca^{++}	0.00	0.01
$N\text{-}NH_4^+$	0.05[2]	0.05[2]
Mg^{++}	0.00	0.00
Na^+	-0.02	-0.02
K^+	0.00	0.01
H_30^+	0.007[2]	0.008[2]
pH	-0.08[2]	-0.06[2]
Standard Gauge Depth (mm)	1.72[2]	1.0[2]
Sample Depth (mm)	2.6[2]	2.0[2]

UNITS IN mg/l EXCEPT pH, SAMPLE DEPTH AND STANDARD GAUGE DEPTH

[1] Median of [CAPMoN - NADP/NTN] differences.

[2] Significant at the 95% confidence level, using the sign test.

TABLE 8.3.4

UDDBC SITING CRITERIA FOR IDENTIFYING REGIONALLY REPRESENTATIVE SITES FROM UDDBC (1985)

1. No continuous industrial source, town or suburban area located within 10 km.
2. No major point source, or combination of point sources, with emissions greater than 10,000 tonnes sulphur dioxide or nitric oxide per year located within 50 km.
3. No surface pollutant storage facility (e.g., salt pile) located within 100 m.
4. No transportation sources, furnaces or incinerators located within 100 m.
5. No cultivation or other agricultural activity within 500 m.
6. No buildings, trees, etc., impinging on a cone defined by a 45 degree angle above the horizontal plane and centred at the collector (30 degrees is preferred).
7. No local area dusty conditions due to poor ground cover.

8.3.4 SUMMARY

From the late 1970s to the late 1980s, the atmospheric research community has expended considerable effort on quality assurance and quality control. Most of this effort has gone into quantifying the accuracy, precision, comparability, completeness and representativeness of the atmospheric measurements, particularly, wet deposition measurements. The results of these activities indicate that wet deposition of the major acidifying species can be measured quite precisely (differences typically less than 5%) and with good comparability (± 25% between networks). Throughout the decade, site representativeness has improved in many Canadian networks, and data completeness has become an important factor in assessing the quality of wet deposition data.

While this chapter has focused largely on quality assurance applied to the measurement of wet deposition, other types of measurement programs have also addressed quality assurance/quality control. This is apparent in the published literature, where almost all Canadian atmospheric research programs have considered quality assurance in their program structure and data analysis.

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8.4 OVERVIEW OF QUALITY ASSURANCE IN TERRESTRIAL RELATED STUDIES

8.4.1 INTRODUCTION

In monitoring and research related to assessment of terrestrial effects of the long range transport of air pollutants (LRTAP), quality control and quality assurance (QA/QC) have not had the profile that they have had in aquatic and atmospheric LRTAP studies. However, most terrestrial studies have incorporated features associated with QA/QC, including formal quality assurance plans, field manuals, duplicate sampling, collocation of sampling, field training, pilot studies, laboratory control programs and inter-laboratory comparisons.

Research activities, which predominate the terrestrial field, tend to have built-in QA/QC components. Since much of this work is destined for formal publication, with associated peer review, emphasis is on development of repeatable methodology, evaluation of equipment, collection of replicate results, assessment of error, and determination of accuracy, precision and reliability.

A few monitoring studies, particularly those initiated within the last three years have been planned with full QA/QC components. However, this has not always been the case. Often quality assurance components have been implemented after study commencement or have been considered informally. Although there are notable exceptions, much of the documentation associated with terrestrial monitoring studies exists in draft form only.

Within the LRTAP Program, terrestrial laboratory quality control programs have lagged slightly behind the water components; however, many laboratories have participated in non-LRTAP interlaboratory programs for both plant and soil material.

8.4.2 TYPES OF TERRESTRIAL STUDIES UNDERTAKEN

Summarizing and assessing the relative usefulness of the approaches that various agencies have taken to QA/QC in terrestrial LRTAP studies is difficult in part because of the wide variety of studies undertaken (Table 8.4.1).

Biogeochemical studies include terrestrial components of the calibrated watershed studies and studies in Ontario, Quebec and the Atlantic Provinces. Monitoring of LRTAP impacts on forest health include a national network of forest plots designed to provide an early warning of declining forest health (Acid Rain National Early Warning System (ARNEWS)); hardwood decline studies in Ontario, Quebec and the Atlantic Provinces; and the North American Maple Project (NAMP), a cooperative project involving the assessment of hardwood health in several northeastern states and eastern provinces.

TABLE 8.4.1

QA CONSIDERATIONS IN CANADIAN TERRESTRIAL LRTAP STUDIES

Study Type and Name	FORMAL QA PLAN	DQO	ERROR SOURCES	PILOT STUDIES	QA MANUAL	DUPLIC. SAMPLES	EXT.COL-[b] LOCATION	INT.COL-[c] LOCATION	BLIND STDS.	INTERLAB[d] COMPARISON
BIOCHEMICAL										
Calibrated Watersheds										
E.L.A.	Y	I	B	-	D	B	-	-	B	B
Bog Acidification	N	B	I	D	B	I	N	N	B	B
Turkey Lakes	Y	B	D	N	B	N	-	-	D	D
Kejimkujik	N	D	D	B	-	D	-	-	D	D
Other										
CFS Que Balsam Fir	Y	D	B	B	-	D	D	D	D	D
CFS Que Sugar Maple	Y	D	B	B	-	D	D	D	D	D
CFS Mar. Nit. Chem.	Y	B	B	B	B	B	-	B	B	B
Hfx Urban Watershed	Lab Only	B	B	-	N	I	-	B	B	B
Nashwaak Watershed	N	B	D	B	N	I	N	D	D	D
OME Canopy Effects	N	I	D	N	D	D	I	D	D	D
OME Forest Soils	N	I	I	I	D	D	N	I	N	B
FOREST ASSESSMENT AND DECLINE STUDIES										
ARNEWS										
Prairies	N	N	I	-	D	N	-	N	D	D
Maritimes	N	B	I	B	B	I	-	-	-	-
B.C.	N	B	I	D	B	N	B	B	I	I
NAMP	Y	B	B/D	N/B	B	B/D	B/N	B/D	-	-
ENVIRONMENT ONTARIO										
Hardwood Survey	N	I	I	N	B	B	N	N	-	-
Dendrochronology	N	I	I	N	B	B	N	N	-	-
Maple Decline	N	B	B	B	D	D	-	-	-	B
Hardwood Nutrition	N	I	I	N	B	B	N	N	N	B
Early Diagnosis	N	I	I	N	N	B	D	D	B	-
Foliage Chemistry	N	I	D	N	D	D	-	-	-	B
Insect Defoliation	N	I	-	-	-	-	-	-	-	-
CFS Maritime										
Cuticle Effects	N	B	B	-	-	-	-	-	-	-
Pollution Effects	N	B/I	D/I	B	B/I	B	B	B	B	B
Maple Decline	N	N	N	B	N	B	N	N	-	-
Mitigation	Y	B	B	B	B	B	-	B	B	B
Birch Assessment	Y	B	I	B	B	-	-	-	-	-

TABLE 8.4.1 (Continued)

QA CONSIDERATIONS IN CANADIAN TERRESTRIAL LRTAP STUDIES

Study Type and Name	FORMAL QA PLAN	DQO	ERROR SOURCES	PILOT STUDIES	QA MANUAL	DUPLIC. SAMPLES	EXT.COL-[b] LOCATION	INT.COL-[c] LOCATION	BLIND STDS	INTERLAB[d] COMPARISON
Other										
Que. Forest Health	Y	B	B	-	B	B	-	B	B	B
ARA (NS)[a] Maple Product Quality	Y	B	D	B	N	B	B	-	D	N
SOILS										
Sensitivity (Ag Can)	N	I	I	-	-	I	I	I	D	B
OME Soil Baseline	Y	N	D	N	D	D	N	N	N	D
OME Soil Variability	N	N	-	N	D	-	N	-	N	-
TRACE METALS										
New Brunswick (DMAE)	N	I	B	N	B	B	-	N	B	N
In Arctic Lichens	N	I	I	-	-	B	-	-	B	-
OTHER										
CFS Maritimes - Air Polution and Plant Reproduction	N	B	D	D	-	B	-	-	-	-

Key

B: Initiated before commencement of study.
D: Initiated during the study proper.
I: Informally considered, but no formal process used.
-: Not available or not applicable.
Y: Yes
N: No
DQO = Setting of Data Quality Objectives

[a] Altantic Research Associates Ltd., Nova Scotia.
[b] External Collocation
[c] Internal Collocation
[d] Interlaboratory Comparison Studies

Notes

All of the above information is based on the replies of the principle investigators of the individual projects and reflect their own perceptions of the QA work which was conducted.

Studies by Agriculture Canada and Environment Ontario have addressed soil sensitivity to acid rain as well as soil baseline characteristics. Forestry Canada, the Atmospheric Environment Service (AES) and several provincial agencies have assessed trace metal deposition from distant sources to lower plants.

8.4.3 HISTORY OF THE DEVELOPMENT OF QUALITY ASSURANCE IN TERRESTRIAL STUDIES

Most early terrestrial LRTAP studies were experimental, phyto-toxicological studies. Quality assurance was and continues to be, incorporated into research programs as part of "good science", hypothesis testing, definition of sources of error and variability, and peer review.

Monitoring studies associated with the early terrestrial effects program usually incorporated stated objectives and documentated methodology into the study plan. Procedures manuals or paper documentation, often in draft form, exist for most if not all projects.

Some individual laboratories began internal quality control programs on terrestrial samples, incorporating testing of National Institute for Science and Technology (NIST) standards as well as blinds, duplicates and blanks. In the late 1970's and again in 1987, the Expert Committee on Soil Surveys generated reference soils data sets with the objective of providing a reference base for participating soil laboratories. Some laboratories participated regularly in intercomparisons such as the International Union of Forestry Research Organization (IUFRO) round robin tests.

Significant monitoring efforts in the late 1970's and early 1980's included the terrestrial components of calibrated watershed studies at Kejimkujik, Turkey Lakes, Montmorency, and Kenora Experimental Lakes Area (ELA). These are principally biogeochemical (nutrient cycling) studies which had already benefited from quality assurance programs in the atmospheric and aquatics fields. Quality assurance plans were prepared for terrestrial components of the ELA and Turkey Lakes watershed studies.

There was very little formal comparison between watershed studies, although common approaches were often used.

In 1985, the ARNEWS was established, with clear objectives and protocols. Although ARNEWS was designed for regional implementation, it was intended that the regional components be directly comparable in terms of site selection and sampling methodology. At the outset of the program methodologies were finalized in an informal pilot study. Most methodologies used had the advantage of having been field tested during routine Forest Insect and Disease Survey Unit (FIDS) field work. Draft manuals were available throughout

the study, with a final manual produced in 1988 (Magasi, 1988a). Sites were frequently co-located with those of provincial agencies.

Studies in maple decline and forest health undertaken by the Ministère de l'Environnement and the Ministère de l'Energie et des Ressources were designed with formal quality assurance plans, use of field methods manuals and attention to the definition of error in the field and the laboratory (Laflamme, 1989). Maple and hardwood decline studies undertaken by Environment Ontario did not include formal quality assurance plans. However during the course of the Ontario studies there has been increasing emphasis on preparation of field manuals (Griffin, 1983; Neary, 1986), use of pilot studies, and definition of sources of error and variability in the field methods used. Both Ontario and Quebec have in-house QA/QC programs and participate in interlaboratory studies.

In 1987, the Quality Assurance Subgroup of the RMCC began to promote awareness of the need for upgrading quality assurance programs in terrestrial monitoring studies. This included preparation of standard methods manuals for analytical procedures for a commonly used group of parameters (in progress), and for field and sampling practices (Site Assessment and Sampling Methodology Ad Hoc Work Group, 1989). There was also establishment of an interlaboratory comparison program for laboratories involved in analyzing samples from terrestrial effects monitoring programs (Quality Assurance Sub-Group of the RMCC, 1989). During the last five years many laboratories participating in such studies have adopted internal QA/QC programs and formal QA/QC plans.

In 1986, Forestry Canada, in cooperation with Environment New Brunswick and several other agencies, began the Fundy Birch Deterioration Project, designed to determine the role of air pollutants in observed deterioration of birch in southwest New Brunswick. This project utilized a pilot study, comparison between agencies of field measurements and sampling, collection of replicate samples, use of CHEF (Chemistry of High Elevation Fog, Atmospheric Environment Service) protocols for collection and analysis of fog water, and collocation of monitoring and biomonitoring systems.

In 1987, the North American Maple Decline Project (NAMP) and an associated quality assurance plan was designed. Throughout the project, there has been careful attention to objectives, formulation, testing and documentation of methods, preparation of a detailed methods manual and training/testing to ensure comparability between groups (Millers, 1988).

8.4.4 QUALITY ASSURANCE/QUALITY CONTROL PROGRAM COMPONENTS

The QA/QC components of specific programs and studies during the last decade are contained in Table 8.4.1 and are discussed in more detail below.
Formal Quality Assurance Plans are present for the NAMP study (Millers, 1988), for some components of the calibrated watershed studies, for Environment Ontario baseline soils study (Neary, 1986; Griffin, 1983), Quebec biogeochemical studies by Forestry Canada (Robitaille, 1989) and for a few research programs. Most laboratories have formal quality assurance plans in place or are in the process of preparing these. Sources of error and variability in some studies have been addressed by use of replicate sampling and submission of duplicates to the laboratory. Pilot studies have been utilized as part of the planning process for the Fundy Birch Deterioration Project, NAMP, ARNEWS and maple decline studies in Ontario, Quebec, Nova Scotia and the Atlantic Provinces.

Collocated sampling within a given project is absolutely essential for assessment of field precision in data collection. The Turkey Lakes Watershed study made use of collocation of both sampling and sampling equipment. NAMP does not collocate sampling efforts within the study, although adjacent states and provinces evaluate plots in adjoining jurisdictions.

Frequently, sampling plots are collocated between agencies, enabling direct comparison of results. An example is the Fundy Birch Deterioration Project where there is collection and evaluation of birch symptomology by a number of researchers with emphasis on comparing methodology. Other examples of collocated plots include Quebec maple decline studies and ARNEWS, NAMP, calibrated watershed studies such as the Turkey Lakes Study, and Environment Ontario's early diagnosis project which makes use of plots already established for other studies.

Field manuals for ARNEWS were developed in a series of working drafts (Jones, 1987; Magasi, 1988b). Field manuals are also available for vegetation sampling carried out by Environment Ontario (Neary, 1986), Environment New Brunswick (Spavold, 1982), the Quebec forest health study (Laflamme, 1989), Environment Ontario baseline and soil variability studies (Griffin, 1983; Neary, 1986), Ontario hardwood decline and biogeochemical studies (Griffin, 1983; Neary, 1986), Turkey Lakes (Morrison, 1989) and NAMP (Millers, 1988). For those programs involving atmospheric measurements in terrestrial studies, manuals are occasionally adopted from other programs, for example in the measurement of fog chemistry for the Fundy Birch Deterioration Project (Cox et al., 1989).

Field audits have not been used in any of the studies outlined above. Most laboratories now participate in interlaboratory comparisons.

8.4.5 RESULTS OF QUALITY ASSURANCE ACTIVITIES

8.4.5.1 Activities Related to the Determination of Accuracy:

Determination of accuracy in field sampling is very difficult due to the lack of appropriate standards with which to compare field measurements. Nevertheless,there have been attempts to measure the accuracy of field measurements. ARNEWS grew out of a program of regular evaluation of forest condition where forecasted forest health problems are regularly checked against results and methods are adjusted if necessary.

Some studies have made efforts to determine accuracy through comparisons of alternative methods of measuring field parameters. For example, in the Fundy Birch Deterioration Project (Cox et al., 1989), these include comparison of active and passive fog collection, calibration of biomonitoring with collocated ozone monitors, and comparisons of percent leaf injury assessed by subjective and quasi-objective techniques.

Standard reference materials are analyzed by most laboratories, either as part of their internal laboratory QA/QC program or, less frequently, submitted to the lab as blind field samples. Most programs make use of standard reference material. A few labs make use of standards prepared in-house, using extensive historical records to determine the variability of the prepared material.

The Expert Committee on Soil Survey has published ranges associated with interlaboratory tests of eight reference soil samples for a wide range of parameters, including pH (two methods), total carbon, organic carbon, nitrogen, particle size distribution, extractable iron, extractable aluminum, exchangeable cations, cation exchange capacity, extractable phosphorus, electrical conductivity, calcium carbonate equivalents, loss on ignition, water retention, and 13 minor elements including cadmium, lead, zinc, nickel, copper, iron, manganese, calcium, magnesium, sodium, potassium, aluminum and chromium (Sheldrick and Wang, 1987).

8.4.5.2 Activities Related to the Determination of Precision:

Most studies have rigorously utilized replicate sampling, at random intervals, and calculated standard errors for the parameters analyzed. Limitations to resources and the numbers of possible samples frequently mean that this is limited to occasional inclusion of duplicate samples, although in calibrated watershed studies, triplicate or more frequent replicates are made. Lichen studies invariably make use of replicates and submission of split samples (Spavold, 1982). Replicate foliage samples are usually collected for evaluation of decline symptomologies.

Replicate sampling is also used to test the precision of field measurements. Forestry Canada FIDS repeats assessments of individual trees. In the Environment Ontario hardwood decline survey, for example, assessments are the consensus of two evaluations. The Ontario dendrochronology survey takes two cores or transects per tree.

Both Forestry Canada and Environment Ontario baseline tree foliage chemistry survey have used replicate measurements to investigate variability from season to season and crown position (Griffin, 1983; Neary, 1986; Morrison, 1972; Morrison, 1974; Morrison, 1985).

In the Fundy Birch Deterioration Project, CHEF protocols are followed for sampling and analysis of fog chemistry, including use of paired fog collectors (Cox et al., 1989). Foliage and crown injury evaluations, as well as other measurements, are also replicated.

A study on the artificial acidification of small upland forested watersheds in the Experimental Lakes Area, focusing on the hydrogeochemical cycling of major ions, submitted random samples to Environment Ontario for comparative analysis (Schindler, 1989).

8.4.5.3 Activities Related to the Determination of Comparability:

One of the principal biases associated with terrestrial field measurements is variation associated with observation and measurement between field technicians. ARNEWS compares the results of one technician to another and has set up comparability studies between adjacent provinces and states to compare measurements. NAMP has also undertaken comparative studies to assess the variation associated with measurement made by one technician and between technicians, as well as between jurisdictions.

Assessment of the health and vigour of tree crowns is particularly subject to observer bias. Environment Ontario has done extensive testing of the reproducibility of the Numerical Decline Index Rating System in the field within and between evaluators (McLaughlin et al., 1988).

The Expert Committee on Soil Survey (Sheldrick and Wang, 1987) has reported results for interlaboratory comparisons of up to 25 laboratories, for eight reference soils, for a wide range of parameters. Extreme results were flagged on the basis of statistical rejection and selected laboratories were advised to check methods and procedures. Percent precision was also calculated for each analytical variable, across all laboratories, according to the method described in Table 8.4.2. Values reported by the laboratories as being below their detection limits were omitted from statistics. The median was used in calculations, rather than the mean, because the median is more robust and has a higher breakdown point (Rousseeuw and LeRoy, 1987). Since the median is not sensitive to one

outlier, and the overal analytical performance was thought to be better evaluated with the inclusion of all data, any potential outliers were included in the analysis.

Interlaboratory variability, as expressed by percent precision, was high for the majority of soil parameters (Table 8.4.2). Relative percent precision for some elements was artificially high due to the nearness of concentrations to the detection limits. Variability does not always decrease linearly as the concentration approaches the detection limit, which results in relatively large standard deviations for small concentration values. There was, however, an inordinate amount of variation for some parameters, given their relatively large values (eg. % sand, % clay, cation exchange capacity). It is unknown whether this variability is due to a lack of adequate quality control in the individual laboratories, or merely to variation in methods used.

For two vegetation interlaboratory comparisons recently completed by the QA Subgroup of the RMCC (Quality Assurance Subgroup of the RMCC, 1989), results were reported for up to eighteen laboratories for audit samples consisting of dried, ground foliage, leaf litter and other test materials. Samples were analyzed for a series of elements including nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, manganese, boron, zinc, copper, molybdenum, chloride, sodium, lead, cadmium, and mercury.

Relative percent precision was also calculated for each parameter measured in the interlaboratory foliage analysis studies (Table 8.4.3). Variability was high, although again some precision estimates were inflated due to the low concentration of a given element. Overall, variation was reduced in study #2 in comparison to study #1, with 13 to 15 parameters having lower percent precision estimates. However, relative percent precision increased in 11 out of 17 parameters during study #3, while only 6 parameters showed any improvement. These studies suggest the need for additional interlaboratory comparisons in order to ensure that data quality continues to improve. Additionally, it is recommended that accuracy of laboratory measurements be monitored.

8.4.5.4 <u>Activities Related to the Determination of Completeness:</u>

Assessments of data completeness are rarely done for terrestrial studies. Data completeness measures have been calculated for measurements associated with the ELA calibrated watershed study (Schindler, 1989) and studies by CFS Quebec (Robitaille, 1989).

In the Fundy Birch Deterioration Project (Cox et al., 1989) the incidence of fog water collections is compared with data on fog events recorded by other agencies to obtain a measure of data completeness.

8.4.5.5 Activities Related to the Determination of Representativeness:

Both ARNEWS and NAMP have documented siting criteria; more specific site criteria are often developed in the various jurisdictions participating in the project. The Fundy Birch Deterioration Project made use of a pilot study year to evaluate the effectiveness of plots from the point of view of representative tree species and the suitability and comparability of sites for assessment of pollutants. Most lichen and bog studies used documented site selection criteria (Spavold, 1982).

8.4.6 SUMMARY

Quality Assurance plans for LRTAP terrestrial components have been initiated but considerable work is still required to fully deploy the systems within all the terrestrial studies.

Terrestrial researchers utilizing water data components should consult the highly developed QA/QC methodologies established in precipitation monitoring or aquatic monitoring programs.

Additional work is required to establish means of determining accuracy of field measurements such as tree measurements, crown condition assessment and other physical measurements and a percentage of measurements and analyses should be repeated.

Laboratories should continue to develop in-house QA/QC programs, participate in interlaboratory comparisons and make widespread use of reference materials. Interlaboratory comparisons are essential for assessing data comparability.

Comprehensive field manuals provide personnel with the proper approaches to sampling and sample handling and allow continuity between investigators or support staff where the study extends beyond one season. Manuals should be developed before sampling commences and, where possible, tested during a pilot study (pilot studies need not be long if they are properly planned) to ensure that recommended methods are practical and finally modified for use in the field. Any changes in methodology should be documented and compared. In order to improve data representativeness, site selection criteria should be established and documented before the commencement of a study. Once they have been chosen, study sites should be described and evaluated to document deviations from the established criteria. Any changes to sites during the course of the study should be documented.

Many of the measurements of the terrestrial effects studies require judgmental observations. In order to improve reliability it is necessary to develop new and appropriate techniques. These would include the use of multiple observers and specially trained observers.

Table 8.4.2

Relative precision of soil chemical measurements[a]

MEASUREMENT	MEAN % PRECISION[b]	OVERALL MEDIAN
pH in H_2O	6.3	6.6
pH in $CaCl_2$	4.0	6.1
% Total carbon	56.7	2.4
% Organic carbon	74.6	1.0
% Nitrogen	28.1	0.1
% Extractable Iron		
citrate dithionate	12.0	0.7
acid ammonium oxalate	43.3	0.2
sodium pyrophosphate	41.3	0.1
% Extractable Aluminum		
citrate dithionate	31.0	0.1
acid ammonium oxalate	32.0	0.2
sodium pyrophosphate	44.5	0.1
Exchangeable Cations (meq/100 g)		
calcium	31.5	4.1
magnesium	116.6	2.4
potassium	38.5	0.2
sodium	49.8	0.1
Bray Extractable Phosphorous (ug/ml)	56.6	9.0
% Sand	74.7	53.2
% Clay	48.6	12.8
Cation Exchange Capacity (meq/100 g)	98.2	21.6

[a]Data were collected from a round-robin carried out by the Land Resource Research Centre, Ottawa (Sheldrick & Wang 1987).

[b]Mean % Precision = mean of 100x $\frac{s_m \text{ for a given sample}}{\text{median of labs for a given sample}}$

where $s_m = \frac{(\text{value - median of labs for given sample})^2}{\text{\# observations on which median is based -1}}$

Table 8.4.3

Relative precision of foliar chemical measurements[a]

MEASUREMENT	MEAN % PRECISION[B] (OVERALL MEDIAN) Study 1	Study 2	Study 3
Aluminum (ug/g)	150.4 (85.0)	55.0 (64.1)	40.9 (74.1)
Boron (ug/g)	39.4 (23.4)	50.2 (19.8)	166.3 (17.5)
Cadmium (ug/g)	--	36.7 (0.2)	75.3 (0.5)
Calcium (mg/g)	19.7 (5.6)	14.9 (5.8)	42.3 (6.1)
Copper (ug/g)	170.4 (7.0)	54.6 (8.5)	30.9 (6.8)
Iron (ug/g)	67.9 (50.0)	36.1 (55.0)	48.4 (51.0)
Lead (ug/g)	129.4 (4.7)	209.5 (2.1)	200.0 (2.7)
Magnesium (mg/g)	69.1 (0.8)	41.1 (1.0)	38.2 (0.9)
Manganese (ug/g)	21.9 (536.5)	14.9 (496.0)	39.9 (490.0)
Mercury (ug/g)	--	148.6 (0.03)	67.1 (0.02)
Molybdenum (ug/g)	--	--	306.3 (1.0)
Nickel (ug/g)	165.6 (1.5)	127.4 (1.6)	282.2 (2.5)
Nitrogen (mg/g)	20.6 (9.0)	17.8 (11.8)	36.9 (11.8)
Phosphorous (mg/g)	73.8 (0.7)	18.7 (1.1)	19.3 (1.1)
Potassium (mg/g)	17.8 (2.7)	10.8 (4.2)	28.7 (4.7)
Sodium (ug/g)	359.0 (42.9)	294.0 (11.3)	147.0 (43.3)
Sulphur (mg/g)	129.2 (0.8)	36.7 (0.9)	47.3 (0.9)
Zinc (ug/g)	147.8 (43.7)	24.0 (33.9)	48.5 (64.0)

[a]Data were obtained from three round-robins prepared for the Federal-Provincial Research and Monitoring Coordinating Committee. These were studies, LTO1, LTO2, and LTO3.

[b]Same calculation as described in Table 8.4.2.

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8.5 OVERVIEW OF QUALITY ASSURANCE IN LABORATORY STUDIES

8.5.1 INTRODUCTION

The external quality assurance program coordinated through the Quality Assurance Subgroup of the Federal-Provincial Research and Monitoring Coordinating Committee was developed in 1982 (Samant, 1982) to overview the quality of data generated by laboratories contributing data to the LRTAP.

The primary element of the external QA program (Hunter, 1980; Aspila et al., 1983 and King, 1985) was the interlaboratory comparison study (Aspila et al., 1989). Three studies have been completed annually. These studies included major ions, nutrients and physical parameters and are listed in Table 8.5.1.

In 1982, the external QA program began with approximately forty participants. In 1985, several U.S. laboratories were invited to participate and the program increased to involve over 100 laboratories. A list of participants is given in Table 8.5.2 of the Appendix 8.5.

In 1987, the program expanded to include one annual study on vegetation and one on soil analysis. These studies, similar to the water program, included about 10 samples and 30 laboratories. The vegetation studies were prepared by the Great Lakes Forestry Centre, Sault Ste. Marie. The one soil study was prepared and evaluated by of the Land Resource Research Centre, Agriculture Canada, Ottawa. One study on soil and three on vegetation have been completed. A third vegetation study is in progress. This assessment report focuses on only the aqueous studies.

8.5.2 THE EXTERNAL QUALITY ASSURANCE PROGRAM

Prior to the conception, development and implementation of an interlaboratory study, a number of factors must be addressed. When a small or large scale environmental program is conceived there is a responsibility of assuring that the program yields credible and traceable data (Hunter, 1980). One element of the management plan (King, 1985) is the external quality assurance program and the associated interlaboratory studies (Aspila, 1983; King 1982; and Aspila, 1989).

An interlaboratory study normally consists of providing an identical set of several test samples to various laboratories for the analysis of specific constituents. Results reported are analyzed (Aspila et al., 1989) and a report is prepared.

TABLE 8.5.1

LRTAP INTERLABORATORY STUDIES COMPLETED (AQUEOUS PHASE)

Study No.	Date Initiated	Subject
L1	Dec. '82	Major Ions, Nutrients, Physicals
L2	Dec. '82	Trace Metals
L3	Apr. '83	Major Ions, Nutrients, Physicals
L4	Aug. '83	Major Ions, Nutrients, Physicals
L5	Dec. '83	Major Ions, Nutrients, Physicals
L6	Apr. '84	Major Ions, Nutrients, Physicals
L7	Aug. '84	Trace Metals
L8	Dec. '84	Major Ions, Nutrients, Physicals
L9	Apr. '85	Major Ions, Nutrients, Physicals
L10	Aug. '85	Major Ions, Nutrients, Physicals
L11	Dec. '85	Major Ions, Nutrients, Physicals
L12	Apr. '86	Major Ions, Nutrients, Physicals
L13	Aug. '86	Total Aluminum and Speciation
L14	Dec. '86	Major Ions, Nutrients, Physicals
L15	Apr. '87	Major Ions, Nutrients, Physicals
L16	Aug. '87	Major Ions, Nutrients, Physicals
L17	Dec. '87	Major Ions, Nutrients, Physicals
L18	Apr. '88	Major Ions, Nutrients, Physicals
L19	Aug. '88	Major Ions, Nutrients, Physicals
L20	Dec. '88	Major Ions, Nutrients, Physicals
L21	Apr. '89	Major Ions, Nutrients, Physicals
L22	Aug. '89	Major Ions, Nutrients, Physicals
L23	Dec. '89	Major Ions, Nutrients, Physicals

The design of a study must be carefully established in order to meet the requirements or objectives outlined in the quality management plan. A successful and well designed interlaboratory study can provide valuable feedback to analysts, lab managers and data users. For instance, the studies may identify (a) overall precision and bias within a laboratory or between laboratories; (b) percent recovery of a constituent; (c) erratic performance; (d) measurement systems that are out of control; (e) measurement systems that have significant baseline errors; (f) blank corrections; (g) failure of a method; (h) operational blunders; (i) inadequacy of intralab QC; (j) inadequacy of internal laboratory standards; (k) adequacy (or inadequacy) of two or more laboratory measurement systems to allow inference that these two systems will produce compatible data bases which are adequate for interagency use; and (l) a neutral third party assessment of the overall performance of a laboratory. Various types of poor and excellent performance in an interlaboratory study are given in Figure 8.5.1. These examples present the situations that external QA programs must review, assess and report on.

A review and assessment of external intercomparison studies have often revealled that internal quality control efforts within a single laboratory are deficient in controlling and defining quality. External studies have provided clear evidence on the comparability of different laboratories and their data bases, detected impure water used in setting instrument baselines (ASTM, 1983), errors in calibration standards and have provided program managers valuable information on contract laboratories (Chau et al., 1987).

8.5.3 RESULTS OF THE EXTERNAL QA INITIATIVE OVER THE PAST TEN YEARS

8.5.3.1 <u>Evaluation of Data</u>:

The techniques to evaluate data in the LRTAP interlaboratory studies were adopted from the International Great Lakes QA Programs using the method of Youden (Youden, 1969) that was modified and computerized by J. Clark (Aspila et al., 1983, Clark 1981). These techniques are now highlighted in a recent QA manual (Aspila et al., 1989). Two simple and distinctly different approaches are used. One method is a nonparametric technique to assess bias (a systematic error) in the whole data set (a parameter matrix of 60 laboratories and 10 samples). The other method is a simple flagging procedure that flags a result if the result reported deviates significantly from the interlaboratory median.

Accuracy in the laboratory measurements are not evaluated directly but rather inferred by the non parametric ranking technique of Youden (Youden 1969). In this technique, results reported are ranked with the lowest, a rank of 1, the second lowest a rank of 2 and so on. The probabilities of ranks are calculated and if the highest average ranks and lowest average ranks are rare events (< 5% chance of occurring) those laboratories are discerned as biased (a systematic error or a relative inaccuracy). There is a 1 chance in 20 of declaring a bias when bias may not exist. The concept of this bias reflecting an

absolute inaccuracy is viewed as valid, since a very large number of laboratories that constantly perform well, have had their laboratories intercalibrated with standard reference materials.

The precision of a laboratory measurement system is not evaluated directly in the external QA program. However, poor intralaboratory precision is quickly recognized from the high percentage of flagged results. A flag is assigned if the result reported deviates significantly from the target value (interlaboratory median). To have no results flagged implies very precise and accurate measurements. To have a large number of flags especially on an ongoing study to study basis implies very poor precision or severe bias.

A satisfactory performance of a laboratory within a study is identified by its ability to be without flags and bias. A computerized technique (Aspila et al., 1989) was used to track the performance over many studies using the sum of the percentage flags and percentage bias as an indicator of performance. An illustration of the track record of one laboratory is given in Fig. 8.5.2.

8.5.3.2 Impact of the External QA Program:

The external QA program provided three (3) interlaboratory comparison studies every year for almost eight years. This regular frequency provided analysts, and managers an opportunity to react to laboratory appraisals. These appraisals indicated that measurement systems were either very satisfactory, out of control, erratic or simply biased and provided motivation for individual laboratory improvements. The overall impact was positive as evident in the case of one laboratory shown as an example in Fig. 8.5.2.

Analysis of the median score of all laboratories from study to study reveals a positive impact over time. The individual results shown in Fig. 8.5.3 are the study median scores and include various parameters. The important issue to note is the almost smooth and continuous decrease in the percentage of flags from one study to the next. This decrease reflects a continuous improvement in precision over time.

Analysis of the frequency of bias is less clear. In study L1, over 30% of parameters were biased. By study L3 and L4, this was reduced to about 12% and remained constant between studies L5 and L21, ranging from 11% to 20%. Two conflicting processes are occurring. Between 1984 and 1989, laboratories became more proficient and improved their accuracy by utilizing standard reference materials. On the other hand, precision also improved and the matrix of parameter data (60 by 10) allowed the non parametric technique to more easily discern systematic difference (i.e. bias). More frequent bias now exists but the magnitude of the bias (systematic error) is now much less severe. This variation in frequency of bias illustrates the relationship of precision and accuracy and the competitive process presented to 100 laboratories who strive for excellence in the interlaboratory study.

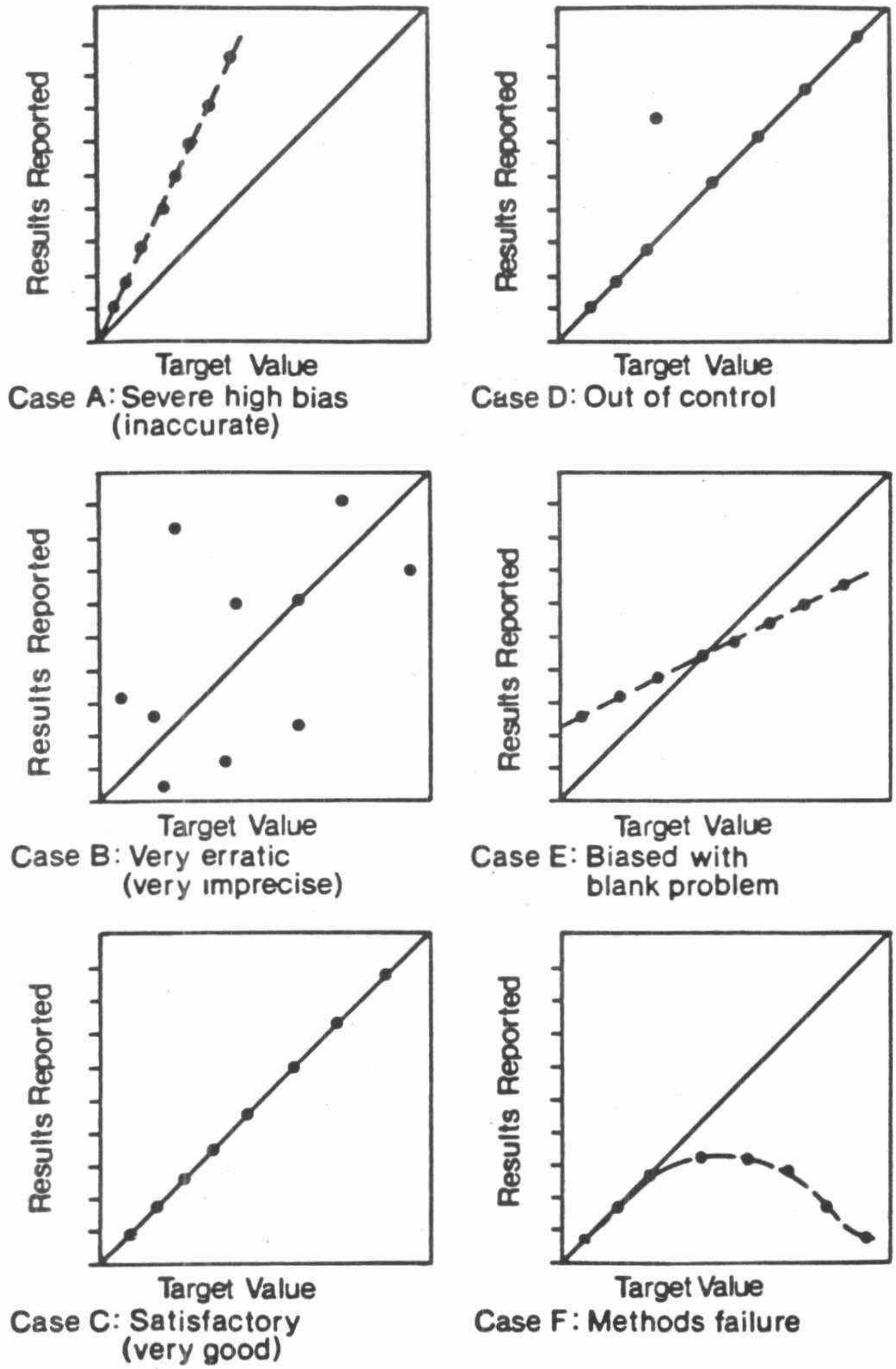

Fig. 8.5.1 Some typical types of Laboratory Performance revealed by External QA Studies.

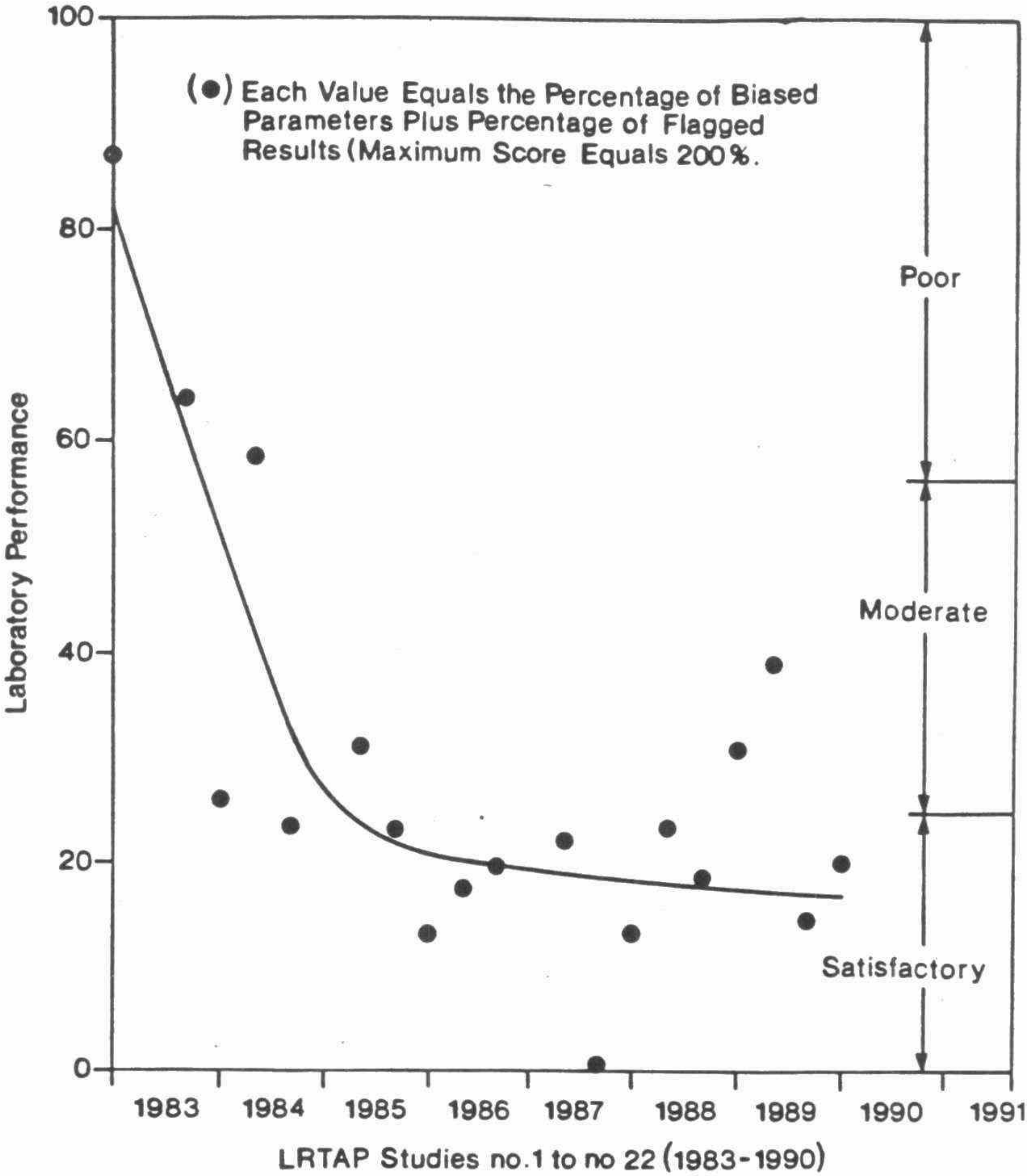

Fig. 8.5.2 Impact of External QA on the Performance of One Laboratory.

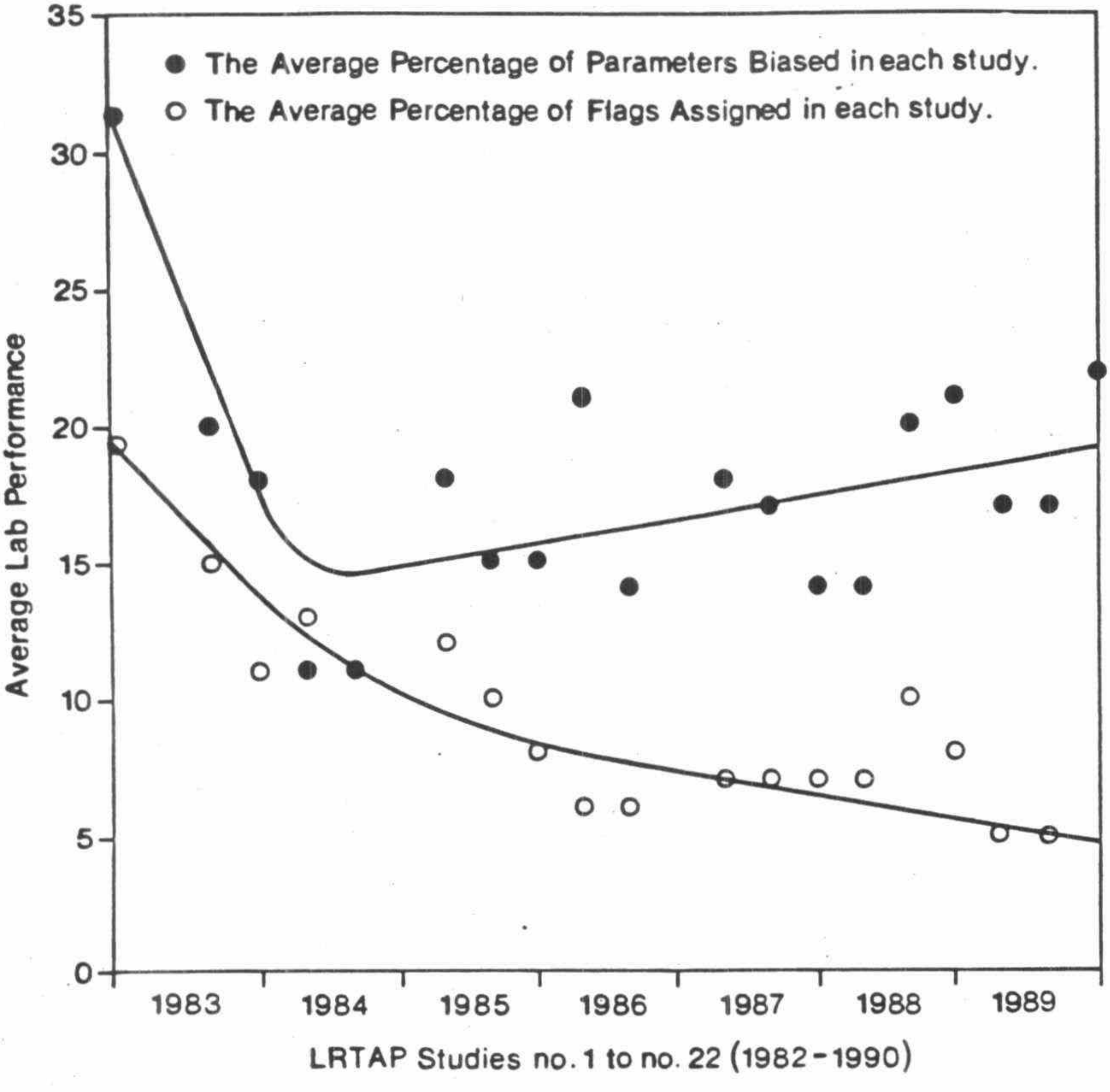

Fig. 8.5.3 Impact of External QA Program on Bias and Flag Frequency.

8.5.4 SUMMARY

The external QA program presented to the LRTAP community by the QA subgroup of the RMCC has primarily addressed issues in the laboratory measurement process. In this area, the program has excelled and has had a positive impact. The presentation of one study every four months for eight years has provided the analyst with an atmosphere conducive to improvement and generated a heightened awareness of QA issues.

Evidence provided in each study has illustrated how many laboratories have clearly improved. Comparability of U.S. and Canadian data is viewed as excellent.

When the QA program was initiated in 1982, a data base management system was adopted to archive all pertinent QA information. It now contains almost a half million laboratory results and is viewed as a valuable resource. The associated software has been instrumental in (a) creating laboratory specific performance appraisals, (b) demonstrating the long term stability of natural water samples and (c) illustrating the ongoing performance of each laboratory on a specific parameter or on a group of parameters. The data base has recently been used to illustrate how precision varies as a function of concentration. Set specific criteria on performance specifications for future studies can now be set.

Although the external QA program has been effective, further areas need to be addressed. These include (a) the monitoring of field and sampling variances, (b) the discernment of laboratory measurement bias on a more absolute basis, and (c) more frequent studies on terrestrial substrates.

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APPENDIX 8.5

LIST OF PARTICIPANTS IN THE LRTAP INTERLABORATORY STUDIES PROGRAM (AQUEOUS PROGRAM).

FEDERAL GOVERNMENT LABORATORIES

Environment Canada

National Water Research Institute, Rivers Research Branch, Burlington, Ontario
National Water Research Institute, Research Support Division, Burlington, Ontario
National Hydrology Research Institute, Saskatoon, Saskatchewan
National Water Quality Laboratory, Burlington, Ontario
Water Quality Branch, Atlantic Region, Moncton, New Brunswick
Water Quality Branch, Quebec Region, Longueuil, Quebec
Water Quality Branch, Western and Northern Region, Saskatoon, Saskatchewan
Water Quality Branch, Pacific and Yukon Region, Vancouver, B.C.
Atmospheric Chemistry Laboratory, AES, Downsview, Ontario
Conservation and Protection Laboratory, St. John's, Newfoundland
Conservation and Protection Laboratory, Dartmouth, Nova Scotia
Conservation and Protection Laboratory, West Vancouver, B.C.

Forestry Canada

Great Lakes Forestry Centre, Sault Ste. Marie, Ontario
Laurentian Forestry Centre, Sainte-Foy, Quebec
Maritime Forestry Centre, Fredericton, New Brunswick
Newfoundland Forestry Centre, St. John's, Newfoundland

Fisheries and Oceans Canada

Freshwater Institute, Winnipeg, Manitoba
Biological Station, St. Andrews, New Brunswick
Institute for Ocean Sciences, Sidney, B.C.
International Pacific Fisheries Commission, Cultus Lake, B.C.
Ministère des Pêches et des Océans, Institut Maurice-Lamontagne, Mont-Joli, Québec

Energy Mines and Resources Canada

Geological Surveys of Canada, Ottawa, Ontario

PROVINCIAL GOVERNMENT LABORATORIES

Alberta Environment, Air Analysis Section, Vegreville, Alberta
Alberta Environment, Water Analysis Section, Vegreville, Alberta
B.C. Ministry of Environment, Vancouver, B.C. (two contract laboratories)
Environment Ontario, Rexdale, Ontario (four laboratories)
Environment Ontario, Thunder Bay, Ontario
Environment Ontario, Dorset, Ontario

Environment New Brunswick, Fredericton, N.B.
Ministère de l'Environnement, Sainte-Foy, Québec
Ministère de l'Energie et des Ressources, Sainte-Foy, Québec
Saskatchewan Research Council, Saskatoon, Saskatchewan
Manitoba Environment, W.M. Ward Technical Services Laboratory, Winnipeg, Manitoba
Nova Scotia Department of Health, Victoria General Hospital, Department of Environmental Chemistry, Halifax, Nova Scotia

INDUSTRIAL LABORATORIES

Atomic Energy of Canada Ltd., Pinawa, Manitoba
Association Industrielle Laval, Pointe-aux-Tremble, Québec
Atomic Energy of Canada Ltd., Chalk River Nuclear Laboratories, Chalk River, Ontario
Barringer Magenta, Rexdale, Ontario
Beak Consultants Ltd., Mississauga, Ontario
Chemex Laboratories (Alberta) Ltd., Calgary, Alberta
Concord Scientific Ltd., Downsview, Ontario
Éco-Recherches (Canada) Inc., Pointe Claire, Québec
Enviroclean, Division of Maclaren Plansearch Inc., London, Ontario
K-F Laboratories Ltd., Fredericton, New Brunswick
Laboratoires d'environnement S.M. Inc., Sherbrooke, Québec
Noranda Mines Ltée., Noranda, Québec
OceanChem Ltd., Dartmouth, Nova Scotia
Ontario Hydro, Etobicoke, Ontario
Roche Envirolab, Sainte-Foy, Quebec
Water Analysis Laboratories, Mount Pearl, Newfoundland
The Environmental Application Group Ltd., Markham, Ontario
Le Groupe Environnemental, Ste. Laurent, Québec
Lab Elite Ltee., Montreal, Québec
Accutest Laboratories Ltd., Nepean, Ontario
Zenon Environmental Inc., Vancouver, B.C.
B.C. Research Corporation, Vancouver, B.C.

UNIVERSITY LABORATORIES

Concordia University, Science and Industrial Research Unit, Montreal, Quebec
Dalhousie University, Trace Analysis Research Centre, Halifax, Nova Scotia
Laval University, Dept. of Geology, Sainte-Foy, Quebec
McMaster University, Dept. of Geology, Hamilton, Ontario
McMaster University, Centre for Neutron Activation Analysis, Hamilton, Ontario
McGill University, Dept. of Geography, Montreal, Quebec
McGill University, MacDonald College, Dept. of Renewable Resources, Ste. Anne de Bellevue, Quebec
Memorial University of Newfoundland, Dept. of Chemistry, St. John's, Newfoundland
Université du Québec, Institut National Researche Scientifique, Complexe Scientifique, Sainte-Foy, Québec
Université du Québec, Dept. of Earth Sciences, Montreal, Québec
University of Montreal, Ecole Polytechnique, Montreal, Quebec
University of Windsor, Great Lakes Institute, Windsor, Ontario

U.S. LABORATORIES

Hunter-ESE, Gainesville, Florida
US Environmental Protection Agency, Central Region Laboratory, Chicago, Illinois, (c/o Bionetics Corporation)
US Environmental Protection Agency, EMSL, Las Vegas (Lockheed-EMSCO)
US Geological Survey, National Water Quality Laboratory, Doraville, Georgia
US Geological Survey, National Water Quality Laboratory, Arvada, Colorado
US Department of Agriculture, Northeastern Forest, Experiment Station, Timber and Watershed Laboratory, Parsons, West Virginia
Combustion Engineering Inc., Environmental Monitoring and Service Inc., Camarillo, California
Illinois State Water Survey, Champaign, Illinois
Battelle, Pacific Northwest Laboratories, Richland, Washington
Lockheed Engineering and Sciences Company, Las Vegas, Nevada
University of Maine, Land and Water Resources Center, Orono, Maine (liaison with Cornell University, Ithaca, New York)
University of Syracuse, Dept. of Civil Engineering, Syracuse, New York
University of Illinois, Dept. of Nuclear Engineering, Urbana, Illinois
University of Minnesota, Dept. of Civil and Mineral Engineering, Minneapolis, Minnesota
Adirondack Lake Survey Corporation, Raybrook, New York
Pennsylvania State University, Environmental Resources Research Institute, Water Chemistry Laboratory, University Park, Pennsylvania
University of Virginia, Department of Environmental Sciences, Charlottesville, Virginia
U.S. Forest Service, Rocky Mountain Forest and Range Experimental Station, Fort Collins, Colorado
Harvard School of Public Health, Dept. of Environmental Studies, Boston, Massachusetts
U.S. Geological Survey, Denver Federal Centre, Lakewood, Colorado
State Lab of Hygiene, Madison, Wisconsin
City of New York, Dept. of Environmental Conservation, Grahamsville, New York
U.S. Geological Survey, Albany, New York
Vermont Dept. of Environmental Conservation, Montpelier, Vermont

BERMUDA

Biological Research Station, St. Georges, Bermuda


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